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THE ORGAN OF THE

Society of Public Analysts and other Analytical Chemists

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OF ANALYTICAL CHEMISTRY

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Errata:

Vol. 59, 1934:

P. 828, line 12. *For* "250 ml." *read* "25 ml."

P. 801. The sentence beginning in the last line should read: "If we take, for example, a 12-stone man who has 100 p.p.m. of lead in his bones, he will have in his whole skeleton 1·5 grms. (23 grains) of lead (as Pb), or 2·9 grms. (31 grains) of lead phosphate, $Pb_3(PO_4)_2$."

Vol. 60:

P. 239, last line of Table II. *For* "6 × 6 ml. H_2O wash" *read* "6 × 10 ml. wash."

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 5th, Professor W. H. Roberts, Vice-President, being in the chair.

Certificates were read in favour of:—Henry Dryerre, Ph.D., M.R.C.S., L.R.C.P., Ronald William Hoff, A.R.C.S., A.I.C., Laurance John Sidney Lane, B.Sc., Alfred Edward Wright.

The following were elected Members of the Society:—Arthur James Amos, Ph.D., B.Sc., A.I.C., Harry Ronald Fleck, A.I.C., Walter Lee, A.I.C., Edward Burdon Parkes, M.Sc., A.I.C., Francis Cecil Storrs, B.Sc., A.I.C., James Thompson, F.I.C., Ph.D., Robert Sinclair Watson, A.I.C.

The following papers were read and discussed:—"The Question of Tannin in Maté," by W. A. Woodard and A. N. Cowland (*Work done under the Society's Analytical Investigation Scheme*); "A Specification for Enamelled Hollow-ware," by J. H. Coste, F.I.C., and D. C. Garratt, B.Sc., Ph.D., F.I.C.; "Antimony Compounds extracted from Enamel-ware by Citric Acid Solutions," by R. H. Burns, B.Sc., A.I.C.; and "Chemical Examination of the Seeds of *Santalum album* of Mysore," by Y. V. S. Iyer.

NORTH OF ENGLAND SECTION

A meeting of the above Section was held in Manchester on December 8th, 1934. The Chairman (Prof. W. H. Roberts) presided over an attendance of thirty-one.

The following papers were read and discussed:—"The Effect of Grinding in the Power Mill on the Albuminoid-content of Feeding Stuffs," by F. Robertson Dodd, F.I.C., and C. Robertson Louden, B.Sc., F.I.C.; "The Examination of Ginger," by G. D. Elsdon, B.Sc., F.I.C., and Catherine Mayne, B.Sc., A.M.C.T.; and "The Hortvet Freezing-point Process for the Examination of Milk: Correction Factors and the Influence of Stirring," by J. R. Stubbs, M.Sc., F.I.C.

Deaths

WITH deep regret we record the deaths of the following members of the Society:

Robert Rattray Tatlock, Past-President (an Obituary Notice will be published later).
Daniel John O'Mahoney (Public Analyst for Cork).
George Egerton Scott-Smith (Public Analyst for Chesterfield).

THE PRESIDENT'S ANNUAL ADDRESS

IN the past it has been customary for the President to deliver an annual address at the end of each year of his office. The Council has considered the matter and has decided that in future the President shall be relieved of having to deliver the first of these addresses, and that in its place some distinguished member of the profession shall be invited to address the Society.

The Council has pleasure in announcing that Dr. Dyer will give the first of these addresses at the Annual General Meeting on March 6th, when he will give some reminiscences of the Society and its members.

The meeting will be at 8 p.m., and Dr. Dyer's address will follow the business proceedings.

DEFINITIONS OF VINEGAR AND MALT VINEGAR

THE following definitions are suggested standards for vinegar and malt vinegar agreed as the result of deliberations between the Society of Public Analysts and Other Analytical Chemists and the Malt Vinegar Brewers' Federation:

(i) Vinegar is a product of the alcoholic and acetous fermentation of a saccharine solution without any intermediate distillation, except in the case of Spirit Vinegar as defined in (iv).

(ii) Malt vinegar should be derived, without intermediate distillation, wholly from malted barley, with or without the addition of entire cereal grain malted or otherwise, the starch of which has been saccharified by the diastase of malt.

(iii) When vinegar is demanded, a purchaser should be supplied with malt vinegar, unless due notification is given to the purchaser of the article supplied.

(iv) The name "Vinegar" may be applied to other products which comply with the definition of vinegar (No. (i) above), provided a prefix is used to denote the origin of the product; thus, "Distilled Vinegar," "Spirit Vinegar."

Distilled vinegar is the product of the distillation of vinegar as defined in No. (i) above, and its source should be denoted; such as, distilled malt vinegar.

Spirit Vinegar is the product of the acetous fermentation of a distilled alcoholic fluid.

(v) "Imitation" or "Artificial" Vinegar should in every case be sold specifically marked "Imitation" or "Artificial" Vinegar. It is any substitute for vinegar containing acetic acid which is not wholly the product of alcoholic and subsequent acetous fermentation, and shall not contain any acid other than acetic acid.

(vi) All Vinegars and Imitation or Artificial Vinegars shall contain not less than 4 per cent. w/v of acetic acid. They shall not contain any acid other than acetic acid or those acids produced by normal fermentative processes.

(vii) Caramel may be used as a colouring matter in all Vinegar and in "Imitation" or "Artificial" Vinegars.

Discussion on Quantitative Spectroscopy and its Analytical Applications

(*Held at the Meeting on November* 7, 1934)

INTRODUCTION

BY J. J. FOX, O.B.E., D.SC., F.I.C.

THE object of the present discussion is to bring before chemists of this Society certain spectroscopic methods now available for everyday use in the laboratory. Modern instruments are convenient to use and capable of giving readily reproducible results. Ever since Bunsen's time the spectroscope has served for the detection of certain elements, and investigation of the ultra-violet spectrum has increased the utility of the method to chemists. Recent work has placed quantitative emission and absorption spectroscopy on a firm basis, so that it is now possible to detect and determine elements and compounds with speed and accuracy. It can be affirmed that among the great advantages of the spectrographic method of analysis are permanency of record, and the fact that in most cases the material examined is available for other tests. It must be borne in mind that the present-day utility of spectrographic methods is due largely to the pioneer work of Mr. Twyman and the firm with which he has been associated in producing instruments of high precision. The papers which follow amply illustrate the scope and accuracy of the method.

GOVERNMENT LABORATORY
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INSTRUMENTS USED FOR SPECTRUM ANALYSIS AND ABSORPTION SPECTROPHOTOMETRY

By F. Twyman, F.Inst.Phys., F.R.S.

It would be interesting to survey the historical steps in the development of spectrum analysis and to enquire why, since the principles of spectrum analysis and the spectroscope were available in 1861, even now, after the lapse of three-quarters of a century, spectroscopic methods are still not in general use by analysts in any part of the world.

Since much ground has to be covered, however, I have confined my remarks strictly to a description of the external features of instruments actually in use to-day for spectrum analysis and absorption spectrophotometry.

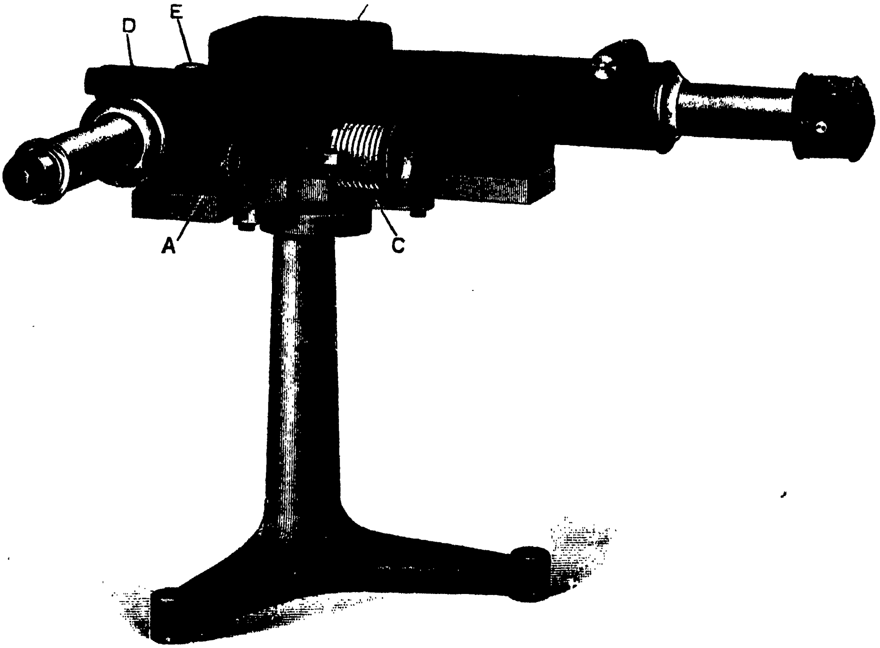

Fig. I
Constant Deviation Wave-length Spectrometer

Spectrum Analysis by Emission Spectra.—For visual work the instrument in general use is the Constant Deviation Wave-length Spectrometer, shown in Fig. I. In this instrument the collimator and telescope are fixed, and the spectrum is traversed past an index in the eyepiece by a screw. To this screw is fixed a drum, C, on which the wave-length of the line under observation is read off directly, as shown in Fig. II. One thus obtains a wave-length scale over a metre in length. Such an instrument is suitable for rapid reference in the chemical laboratory.

Most of those who practise spectrum analysis use a quartz spectrograph, which photographs not only the part of the spectrum from wave-length 400 to

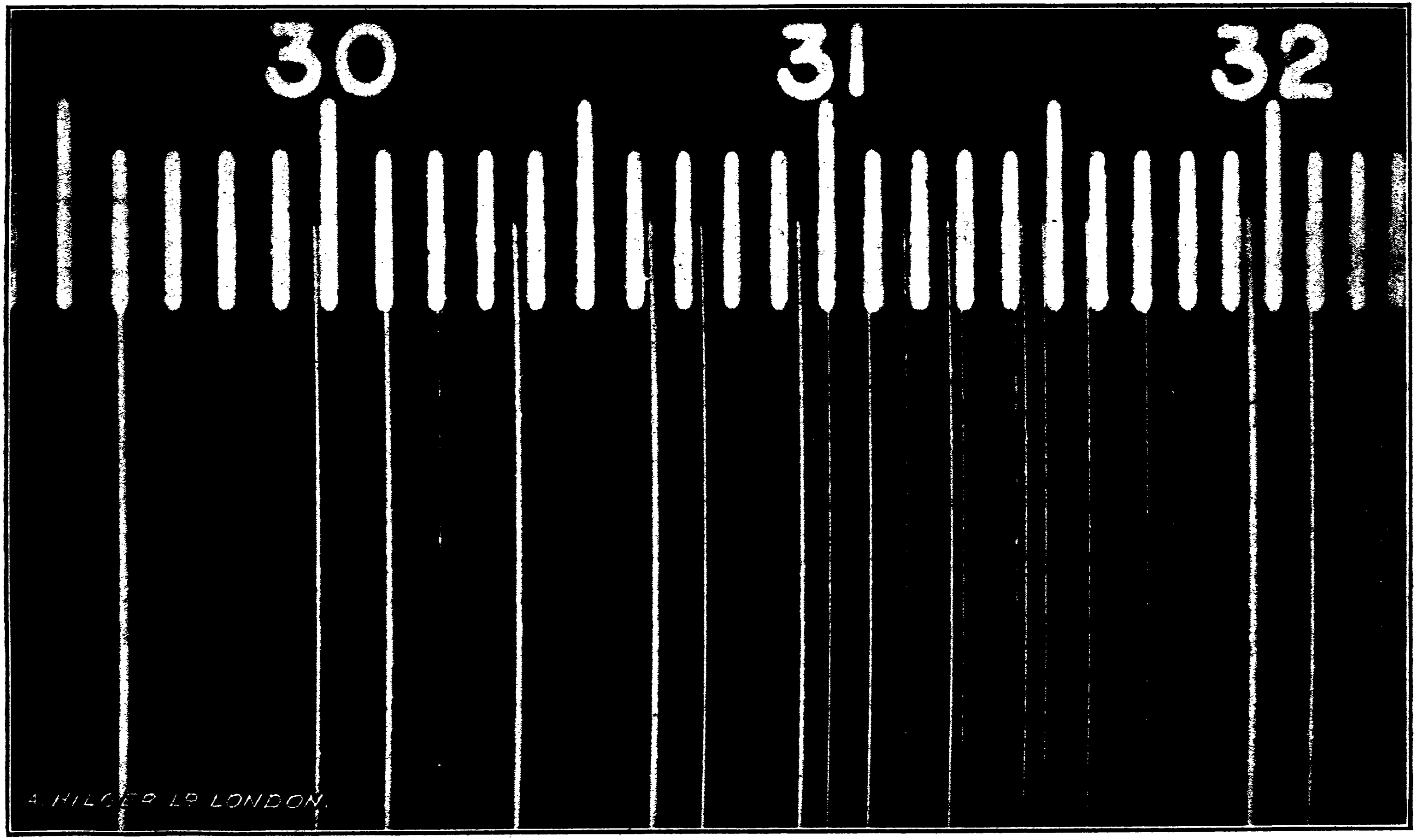

Fig. IV
Spectrum with wave-length scale

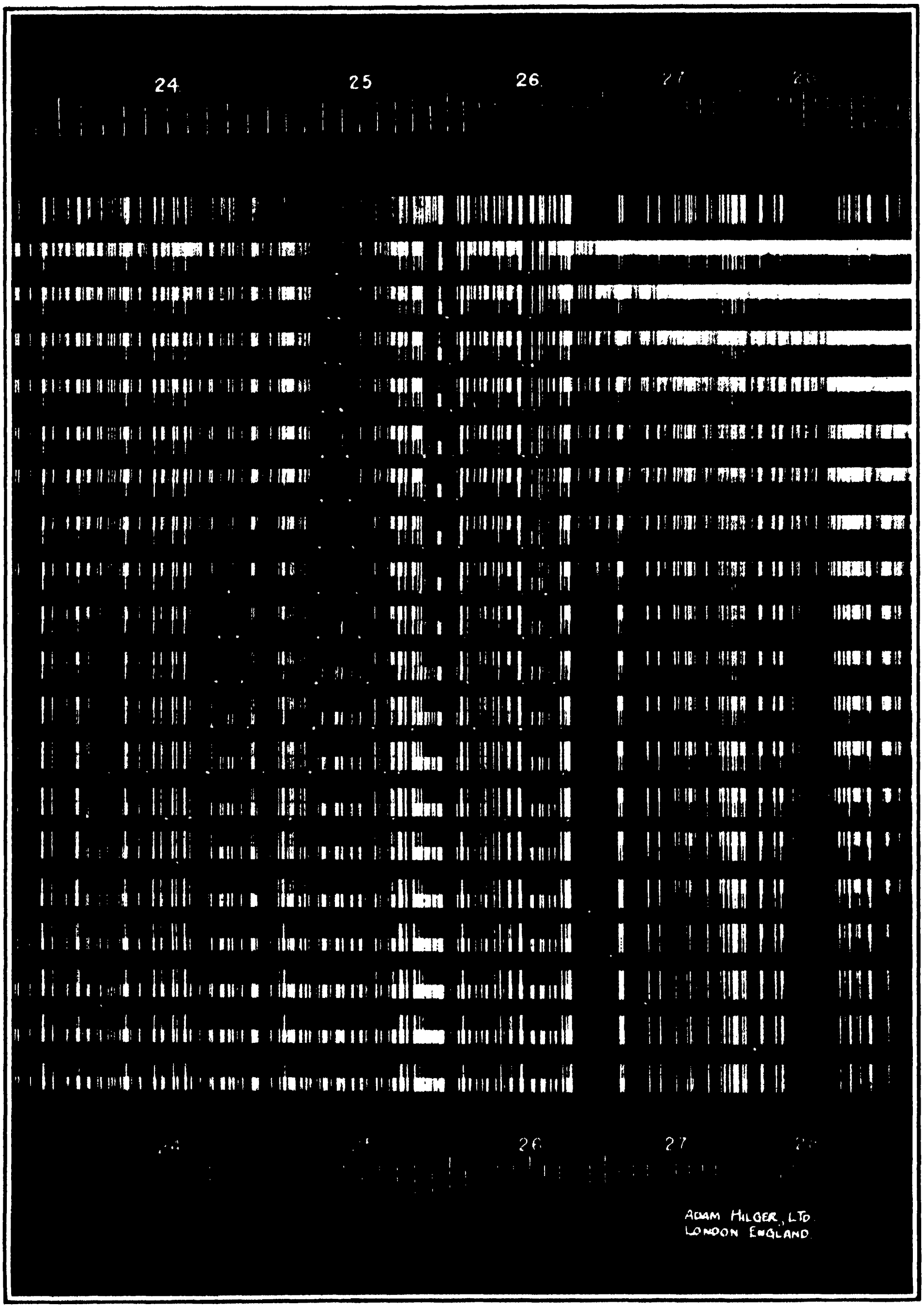

Fig. IX.
Photograph taken with Spekker Photometer

about 819$m\mu$ visible to the eye, but also the range of ultra-violet spectrum from wave-length 200 to 400$m\mu$.

The type of quartz spectrograph used for spectrum analysis is shown in Fig. III. This instrument is adjusted once for all, and to take photographs with it is no more difficult than to do so with a hand-camera. A handle at the side serves to raise and lower the dark slide, and 15 or 20 different spectra can conveniently be taken on one plate. A wave-length scale can be printed on the spectrum and is developed with the spectrum itself. The spectrum is shown in Fig. IV.

Such an instrument, with which the whole spectrum can be taken on a single photographic plate (10″ × 8″), is the most convenient size for general chemical work. It is often referred to as a "medium-size" quartz spectrograph, but it is preferable to distinguish the size by the focal length of the camera lens for a specified wave-length—in the present case 60-cm. focus for wave-length 589$m\mu$.

A larger size, having three times the dispersion, is made, but this requires a number of separate exposures to cover the whole range of the spectrum. Such dispersion is seldom necessary in spectrum analysis, if we except the analysis of steels.

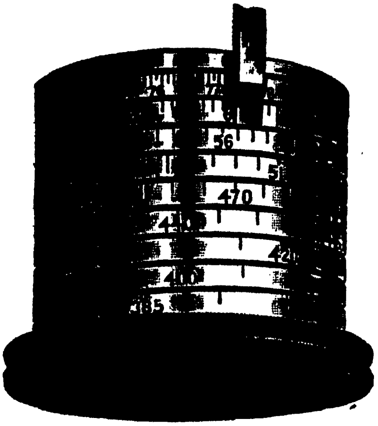

Fig. II
Wave-length Drum

A small instrument, having one-third the dispersion of the medium one, is very useful in metallurgical work for the examination of metals with simple spectra, such as brasses, bronzes, lead alloys and so forth; it was used by Mr. D. M. Smith in the work described in his paper (see p. 17).

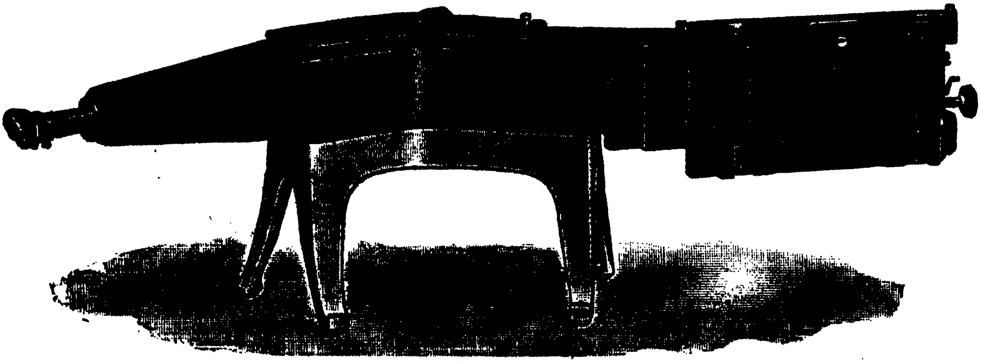

Fig. III
Quartz Spectrograph, 60 cm. focus

ACCESSORIES.—Arcs of the metals are very easily produced, provided that direct current is available. Pieces of the metal are used as electrodes; a direct current of 3 amp. or more produces an arc that will reveal all the constituent metals. Small pieces of metal or other samples, such as powders, filtered precipitates, dry residues from solutions, etc., can be examined by putting them in the scooped-out lower carbon electrode of an arc. One advantage of the carbon arc is that, unlike metallic arcs, it can be used with an alternating current.

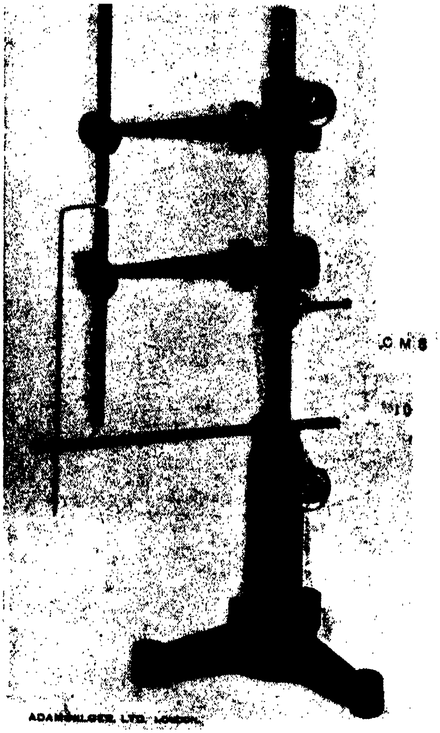

Fig. V
Gramont Arc or Spark Stand

Numerous other ways of using the arc are available, but, whatever method of producing the arc-discharge is adopted, a suitable form of lamp is that known as the Gramont Arc or Spark Stand (Fig. V), since it is equally suitable for using with the spark. The distinctive feature of the Gramont Stand is that, after the arc or spark has been adjusted to a suitable length, the stand can be raised and lowered by means of a rack and pinion, and thus aligned with the spectrograph without disturbing the discharge.

For some purposes the spark is better than the arc, and the best way of obtaining it is from a ¼-kilowatt transformer giving secondary voltages of from 8000 to 15,000 on an open circuit. With the transformer are associated a condenser and a self-induction coil of simple character.

Accessories for Quantitative Spectrum Analysis.—All endeavours to make spectrum analysis quantitative in character depend on the fact that, the greater the percentage of a metal in a sample, the stronger will be the spectrum lines of that metal. Perhaps the most useful method of rendering spectrum analysis quantitative is to synthesise a specimen so that its spectrum exactly matches that of the sample. This method has been very fully worked out by Judd Lewis. It needs no instrumental accessory except a convenient means of comparing the spectra, and this is provided by the Judd Lewis Comparator. The Microphotometer has been used by some observers to measure the intensities of the lines, and with due care it can yield valuable and very accurate results.

In my opinion, the apparatus which, at the present time, best combines convenience and accuracy is the Logarithmic Sector (Fig. VI).[1] This instrument is a disc of metal, the periphery of which is cut into the shape of a logarithmic spiral. This is rotated in front of the slit, and, if the shape of the spiral is properly selected, the effect is to produce on the plate spectrum lines, the differences in the lengths of which are in proportion to the logarithms of the relative intensities of the corresponding radiations. Fig. VII shows the appearance of such photographs.

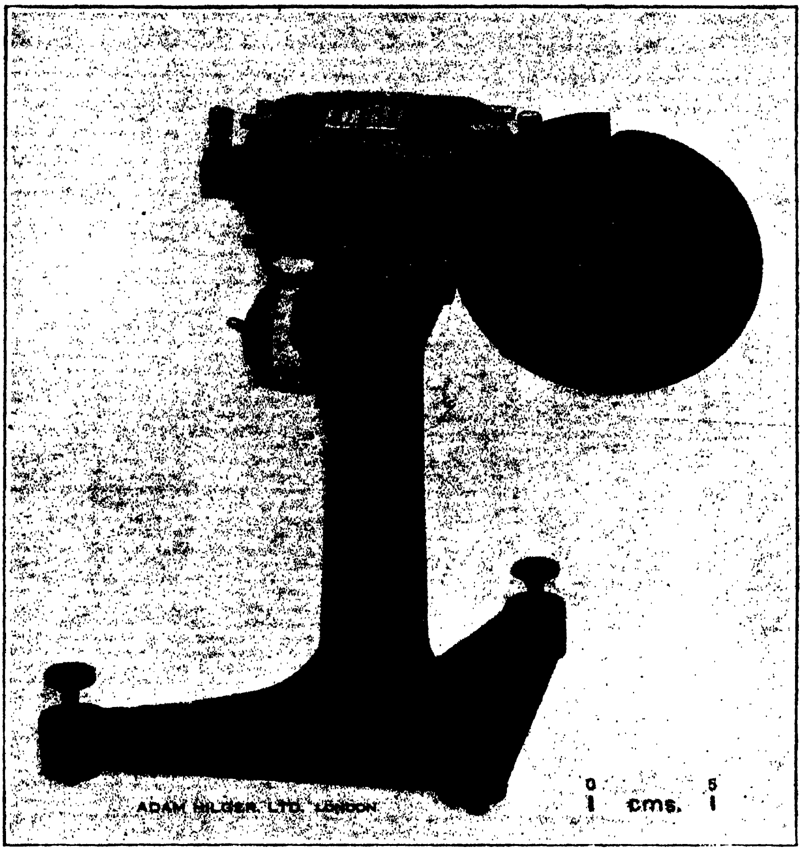

Fig. VI
Logarithmic Sector

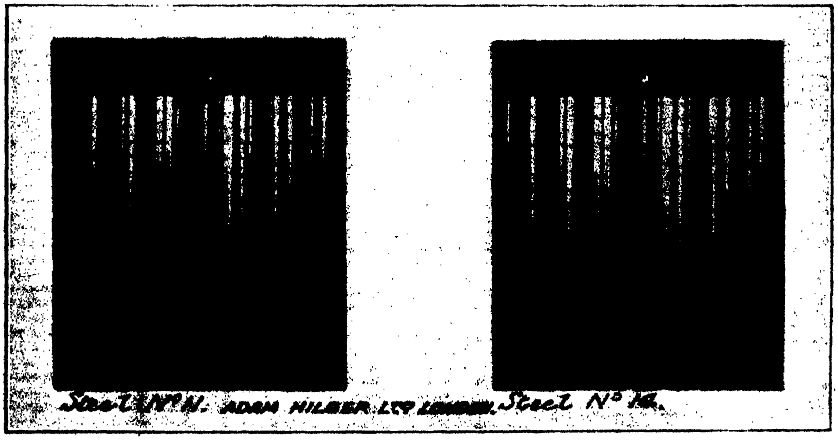

Fig. VII
Spectra taken with Logarithmic Sector

APPARATUS FOR ABSORPTION SPECTROPHOTOMETRY.—Absorption spectrophotometry means the measurement of the absorption of radiation by a substance for various wave-lengths, so that a curve of absorption may be plotted. Such a curve is often highly characteristic of the substance (see Fig. X). The simplest way of doing this is by means of the apparatus, known as the Sector Photometer, which I introduced about 1912. A large proportion of the work on ultra-violet spectrophotometry, in various parts of the world, has been done with this instrument, but this is now superseded by a simplified form of Judd Lewis's spectrophotometer (shown in Fig. VIII), which is known as the "Spekker" Spectrophotometer.[2] It is intended to be placed in front of a spectrograph, such as a quartz spectrograph. Light from a suitable source of ultra-violet rays (A) passes towards the inner edges of two quartz rhombs, C, C, from which beams are diverted upwards and downwards, to be reflected forward through the tubes, F, F, in one of which is placed the absorbing liquid, and in the other the liquid with which comparison is to be made. For instance, in the one tube there may be an organic substance in a solvent, and in the other tube the solvent alone. The beams from the rhombs pass, the one through a fixed rectangular aperture, and the other through an aperture the size of which can be varied by means of a micrometer screw, rotated by a drum, D, with an index which travels along a helix in the drum. This not only simplifies readings, but also acts as a stop to prevent the drum from being turned too far in either direction.

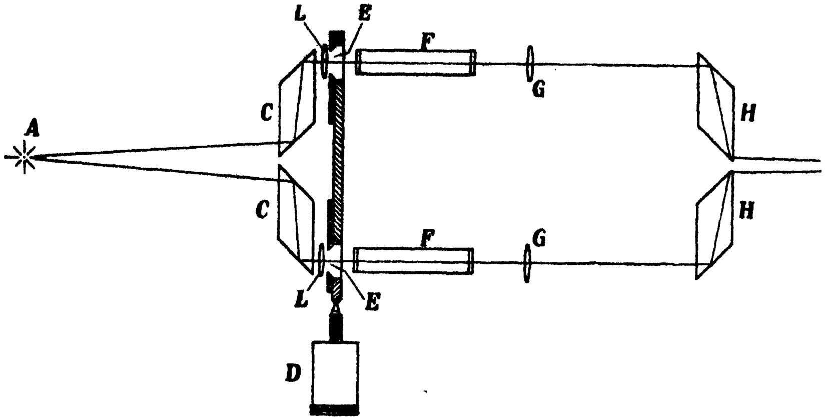

Fig. VIII
Diagram of "Spekker" Spectrophotometer

After passing through the absorbing substance and the non-absorbing substances, the beams pass through lenses, G, G, of quartz, the focal length of which is such that an image of the light source is formed on the face of the slit of the spectrograph. A second pair of quartz rhombs, H, H, is arranged to bring the beams of light together on to the slit in such a way that the image falling from the top rhomb and that from the bottom rhomb on the slit form a complete image of the light source. A number of photographs are taken, one below the other, with various widths of the adjustable aperture (see Fig. IX).

It will be seen that there are a number of pairs of spectra, one spectrum of each pair being cut down in intensity uniformly along its length by a known amount, whilst the other has its intensity locally reduced by reason of the absorption of the liquid under examination. There are certain places, indicated by spots in the figure, where the two spectra match, and at these points, if we know the width of the aperture, we can deduce the absorption of the liquid.

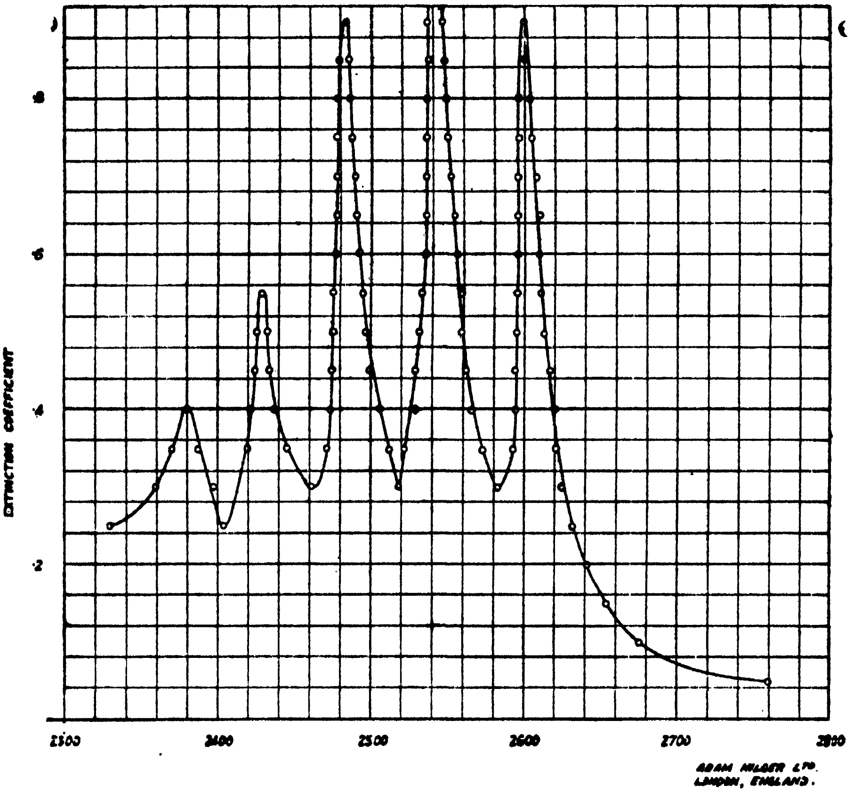

Fig. X.
Absorption Curve of Benzene (in Hexane)

Fig. X shows a curve drawn from the values obtained from the preceding photograph; it is the absorption spectrum of benzene in hexane, 1 in 3300.

References

1. F. Twyman and F. Simeon, *Trans. Opt. Soc.*, 1929–30, **31**, No. 4.
2. F. Twyman, *Trans. Opt. Soc.*, 1931–32, **33**, No. 1.

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QUANTITATIVE SPECTROSCOPY AND ITS ANALYTICAL APPLICATIONS

BY S. JUDD LEWIS, D.Sc., PH.D., F.I.C.

This discussion is concerned with those aspects of the subject which are of direct practical concern to the analytical and consulting chemist in general practice, rather than to those following any particular branch of the subject.

In Mr. Smith's contribution (p. 17) it will be found that it is possible to work with metals in the compact form, and that everything makes for success. On the other hand, non-metallurgical materials, such as the ashes of plants or of textiles or the total solids of a water or a milk, offer none of these advantages. They are usually much less homogeneous than alloys, they are frequently incapable of taking any convenient shape, they are usually inferior conductors of electricity, and they function very irregularly under the influence of any electric discharge. Moreover, it is desirable to work by the arc method rather than by the spark, and here one meets with difficulty of another kind, namely, the wandering and irregular functioning of the arc.

The problem, then, is to formulate some method which will be suitable for such very heterogeneous materials, and this has been done, with a very fair measure of success, in the Ratio Quantitative System, of which I have already given a description.[1] Although the present paper is mainly concerned with the details of this system, one must not lose sight of the excellent *Flame* work of Lundegardh[2] of Stockholm, in dealing with plant ashes and the like. He passes a blast of air through a solution of the ash, contained in the well of a perfume spray of particular form, into an acetylene blow-pipe, where the mixture is burnt in front of the slit of a spectrograph. A spectrogram rich in the lines of a limited range of elements is produced. Every detail is rigorously controlled.

Hartley's method for sparking solutions has been greatly improved of late by Twyman and Hitchen.[3] Mention should also be made of the method of saturating a soft carbon electrode with the solution in question, and arcing on alternating current; also of Ramage's method[4] of burning a weighed quantity of the substance in a rolled filter-paper in an oxy-hydrogen flame.

The reasons for laying stress upon the Ratio Quantitative System by the Arc method are:—(i) It is new; (ii) it is directly applicable to materials of *every* type to an extent not possible with any other method; (iii) it is easily controlled and rendered efficient without resort to special photometric equipment or other special devices; (iv) it records a *complete* quantitative survey of *all* the metallic elements composing the sample, even when the quantity of material is very small; 5 mg. is the normal load, but if one has only 1 mg., or even less, of the sample, the method is still valid, if a like quantity of the standard is used for the comparison; (v) it is applicable both to soluble and insoluble substances.

The conception of " Ratio " is merely mathematical, but in its application to quantitative spectrum analysis the idea is that, if one knows the proportion of a minor element in terms of ratio or percentage to that of a major component, the proportion of which is either known or ascertainable chemically or spectroscopically, one knows the proportion of the minor element in the sample.

For example, if there is in the total solids of a water 0·017 per cent. of manganese relative to calcium, and there are 10 parts of calcium per 100,000 in the water, there is 0·0017 part of manganese per 100,000 in the water.

Moreover, the ratio idea permits of still wider application, for if the ratio of manganese to calcium in the ash of a plant is known, it is known also in the plant or other biological material from which the ash was prepared.

Experimentally, the basic ideas are: (i) To bring the whole sample of ash or other material into some constant homogeneous condition; (ii) to arc (or spark) under well-defined uniform control. The first of these requirements is satisfied by converting the ash into sulphates according to prescription, and the second by well-controlled experimental procedure in order to render the work constant and comparable.

A portion of the vegetable ash, including any phosphate, silicate or other insoluble matter which it may contain, is treated with a small excess of sulphuric acid in a new silica crucible. The mixture is evaporated and gently ignited, just sufficiently to drive off the excess of sulphuric acid. Thus the whole mass is in a condition approximating to normal sulphates, "homogeneously" mixed with the pre-existing phosphates, silica, etc. It is then mixed with an equal weight of spectroscopically pure ammonium sulphate, and is ready for spectrographing.

The use of ammonium sulphate secures three or four advantages: (i) It supplies in effect a constant amount of sulphuric acid to the mass; (ii) it renders the mass more porous; (iii) it generally helps to regularise the action when a portion of the mixture is burnt in the arc.

Ten mg. of the mixture are placed on the lower electrode of a suitable arc-lamp, set in front of the slit of the spectrograph. The next step, *viz.* that of "striking" the arc and exposing the mixture for a suitable time, *e.g.* 60 seconds, is the critical operation; it must be controlled with great care if constant, comparable results are to be obtained. After development of the photograph in the usual way, the first spectrogram is obtained. The same procedure is followed with 10 mg. of a suitable standard ratio powder, and thus a second spectrogram is obtained; in practice, however, this operation is eliminated, since it has already been done once for all. The two spectra are then compared in a "Comparator."[1]

An inspection of the spectrogram of the ash will at once reveal its approximate composition, that is to say, it will be obvious that it is mainly sodium or potassium with much or little calcium and magnesium (or *vice-versa*), together with more or less phosphorus, silicon, etc., and one can then take from the file a standard spectrogram of a suitable ratio powder to serve as standard for comparison.

Assume the major metallic element to be calcium, and consider three standard ratio powders having calcium as a base and containing manganese, lead and tin: (*a*) With 1 per cent. of each element relative to calcium; (*b*) 0·1 per cent.; (*c*) 0·01 per cent.

On comparison of the intensities of the manganese, lead and tin lines in the spectrum of the unknown mixture with those, respectively, in each of these standard spectra in turn, one is able to determine that the manganese is just a little stronger than 0·1 per cent. or about 0·11 per cent.; that the lead is about one-third of 0·1 per cent., and three times 0·01 per cent.; therefore, that the lead is about 0·03 per cent.; and that the tin is a little less than 0·01 per cent., approximately 0·008 per cent. This principle is founded on both theory and laboratory experience. In using a correct mixing a condition of experiment is attained, which justifies usually, although possibly not always, comparison of "homologous pairs" of lines by the "internal standard" method, using for reference the lines of the main component, not those of the electrodes.

Preparation of Special Ratio Powders.—If more precise results are desired, a special ratio powder may be prepared in accordance with these findings, and then the deviation in each case should be so small that any remaining differences may be estimated by inspection.

If still more exact figures are required, they may be obtained by repeating the determination with the quantities as estimated in the second experiment.

As already intimated, this synthesis of a special standard is the systematic and final step, but by comparing the unknown with stock ratio powders, one can, for many purposes, obtain readings sufficiently close without making the synthetic mixture. It must, however, be emphasised that in the final appeal, one should have the major elements in approximately the correct proportion, since the intensity of the lines of the minor element is not precisely the same when the base is mainly calcium, as it is when the base is mainly sodium; and so on.

This sounds, perhaps, a little lengthy, but in practice it is not so, for standard "Specpure" solutions are already available commercially. It must not be assumed, however, that accurate quantitative comparisons can be made until one has acquired some experience.

A most important feature of this method is that it economises time, for *each one* of these determinations applies to the *whole range* of elements concerned, major as well as minor, and *not*, as in most chemical work, to one only. Thus, in making the synthetic mixture one adjusts, by measuring out appropriate quantities of the solutions of the several metals, the proportion of each one of the elements, and so, in the end, one finds that the synthesised spectrum is practically identical in all respects with that of the unknown ash.

ACCURACY OF THE PROCESS.—It remains to show what order of accuracy may be expected from such work, and in order to avoid uncertainty or unconscious bias, determinations controlled by chemical work in other laboratories have been selected.

(i) *Iron in Aluminium.*—The determination of iron in aluminium by chemical processes is frequently a matter of great uncertainty—so much so, that several chemists have resorted to spectrographic methods of one kind or another, and claim greater uniformity of result. With two samples the following percentages were obtained by myself and my assistant, Mr. F. W. J. Garton, respectively, (*a*) by the adopted method, (*b*) by a distinctly modified method, to see whether a marked difference of procedure prejudiced the results seriously.

	No. 1.			No. 2.		
	Adopted method Per Cent.	Modified method Per Cent.	Difference Per Cent.	Adopted method Per Cent.	Modified method Per Cent.	Difference Per Cent.
By S.J.L. ..	0·083	0·080	0·003	0·101	0·089	0·012
By assistant ..	0·088	0·087	0·001	0·097	0·092	0·005
Difference ..	0·005	0·007		0·004	0·003	

These readings are all first-hand laboratory results without subsequent adjustment.

(ii) *Vanadium in Organic Material.*—The next example shows that similar tolerance applies to major components, as exemplified by vanadium in the ash from an industrial organic material, of which only a few mg. were available.

	Spectroscopic Per Cent.	Chemical Per Cent.
Vanadium, as metal	26·6	26·2
	14·5	13·0

With smaller proportions of vanadium the results also agreed well, *e.g.* 0·75, 0·76; 0·80, 0·81, 0·77; 0·71, 0·74 per cent.; these three samples were not controlled chemically.

(iii) *Nickel in Organic Material.*—Similarly, nickel in an organic material was controlled.

	Spectroscopic Per Cent.	Chemical Per Cent.
Nickel, as metal	3·5	3·0
	3·6	3·3

Whilst these figures demonstrate that consistent results are obtainable spectrographically, and that they are closely comparable with those determined chemically, they afford no evidence as to which method is to be preferred. The following investigation with copper tends to favour the spectrographic method, since it is free from complications which beset the chemical method.

(iv) *Copper in a Food.*—The following results, in parts per million, were obtained:

	Spectrographic	Chemical
	0·46	0·56
	0·46	0·56
	0·49	0·56
	0·50	0·56
	0·48	0·53
	0·63	0·68
Duplicates	0·33, 0·33	—
	0·32, 0·36	—
	0·33, 0·29	—

As the chemical findings depended upon the removal of lead in an earlier stage of the process, it is quite possible that the results in the subsequent colorimetric determination of copper may be a little high, owing to incomplete removal of lead.

The following examples illustrate work of a somewhat different class:

(v) *Germanium.*—Germanium, when present in zinc to the extent of only one part in 100 millions, may be estimated quite well by dissolving 5 g. of the zinc in acid and co-precipitating with a suitable heavy metal by means of hydrogen sulphide, filtering, and incorporating homogeneously a little calcium to serve as the standard base, then spectrographing in accordance with the Ratio Quantitative System, and comparing the arc spectrograms with a special standard of Ge/Ca.

(vi) *Biological Fluid.*—Aqueous humour, 0·28 g., yielded 3·5 mg. of sulphated ash, containing about 1 mg. of mixed alkali metals, which was spectrographed with a known weight of spectroscopically pure calcium chloride; upon determining the ratios Na/Ca and K/Ca, it was found that the ratio NaCl/KCl was 15: 1. We have no figures for human aqueous humour, but for the horse the ratio 22 : 1 has been found.[5]

Apart from the ratio method, it has also been shown in detail how 1 part of aluminium can be determined in one million of blood with a very fair approximation to the truth, when using only a single ml. of blood, and, as the result of several experiments on the human subject, it has been found that the blood becomes saturated with aluminium at about that concentration.[6] Reference to the same spectrograms reveals the fact that silicon (in traces only), lead, boron, arsenic, tin, and zinc are among the elements frequently occurring, and that manganese, strontium, barium, and silver are present in only minute quantity, or not at all. By following up these observations quantitatively much light may be thrown on problems depending on the inorganic chemistry of blood.

APPLICATION OF SPECTROSCOPY TO CRIMINOLOGY.—Occasionally spectroscopy has been applied to criminology, as illustrated by the following cases:

(i) The case of the "affaire de la Bonnet Rouge." On the boot-lace of the criminal Almereida, who died mysteriously in the infirmary, two stains were found. M. Bayle was asked to analyse these stains. By comparison of the spectra of: (*a*) the unsoiled part of the boot-lace, (*b*) the two stains, (*c*) the paint on the bedstead in which Almereida had slept, it was shown that one of the stains was due to mud, and the other to paint from the bedstead. The spectrum of the first stain showed aluminium lines, whilst that of the other stain showed the lines of barium, zinc and lead in exactly the same way as did the spectrum of the paint. This gave the police the required information, and confirmed the conclusion that Almereida had hanged himself in prison.[7]

(ii) Wilson,[8] writing in the *Journal of Criminal Law and Criminology*, complains that spectroscopy has not yet found the wide use it deserves in criminal investigation, and then proceeds to describe two or three interesting cases. In one of these the spectrographic analysis of a slight smear on a coat was identified with the putty from a window broken during a burglary, and led to the man's conviction.

(iii) Telephone wire stolen from a Government department in Ceylon was identified spectroscopically as containing traces of certain ingredients which were present in Government stock, but not in any other samples obtained locally.[10]

(iv) In another case, also from Ceylon: "17 lead pellets and slugs were examined spectroscopically, and were found to consist of five different types of lead. The same five types of lead found in these pellets from the scene of the crime were all represented in the pellets, etc., found later with the weapon which was suspected of having been used."[9]

One must anticipate that the question will arise: How far can evidence of the spectroscope be acceptable in a court of law? I have not considered this question exhaustively, but my impression is that the spectroscope will provide very strong evidence when the analyst has become so familiar with the work that he can, with absolute conviction, swear to the results he obtains. I believe that then the evidence will be more readily accepted than is much of the chemical work, since the results may be demonstrated in photographed spectra.

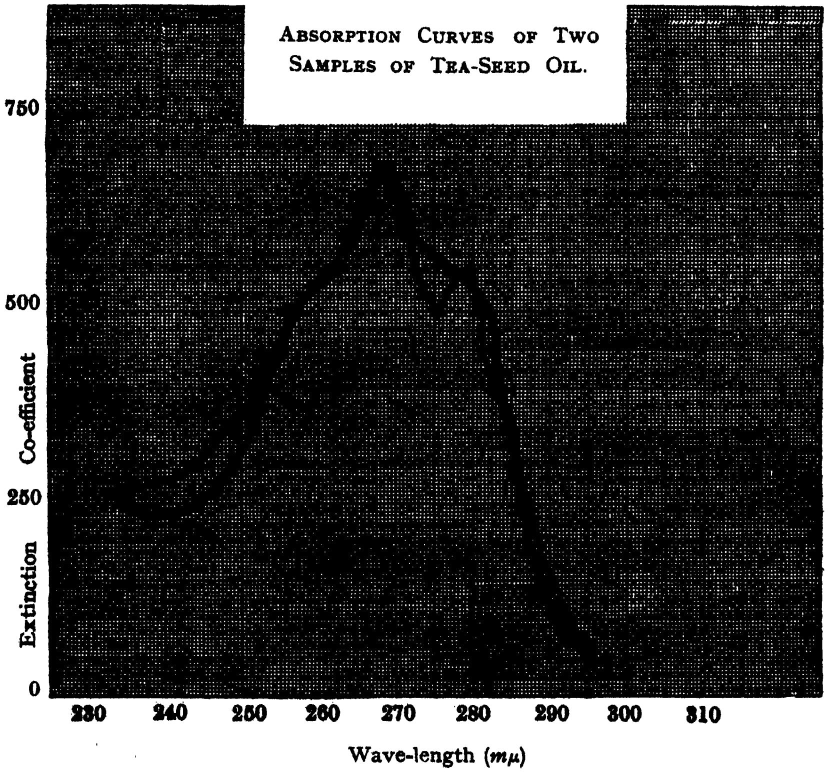

Fig. I

ABSORPTION SPECTROSCOPY.—As time does not permit of a full description, I must ask you to allow half-a-dozen slides to speak for themselves.*

The absorption curve of a special glass exhibited the narrow bands due to neodymium at 332, 425, 436, 502, and 575$m\mu$, and to praseodymium at 444, 467, and 480$m\mu$, just as would a solution of salts of the two elements. This method of investigating the absorption spectra of the rare earths by spectrophotometry affords the best and most reliable means of analysing quantitatively mixtures of these and certain other elements.

* Those shown were Figures 29, 30, 31, 32, 38, 39, in *Spectroscopy in Science and Industry*, by S. Judd Lewis (Blackie).

Spectroscopic Detection of Tea-seed Oil in Olive Oil.—The last slide demonstrated the detection of tea-seed oil in olive oil by means of absorption spectroscopy. In Fig. I (p. 15) are seen curves for two samples of tea-seed oil, and in Fig. II the absorption curves for (A) pure olive oil and (B) and (C) the same olive oil to which has been added 1 per cent. and 5 per cent., respectively, of tea-seed oil. It should be observed that the extinction coefficient of olive oil at a wave-length of 268*mμ* is 11, whilst that of tea-seed oil is 690, and that of the 5 per cent. mixture 46, which is in good accord with the calculated figure, 690 × 0·05 + 11 × 0·95 = 45; similarly, the mixture containing 1 per cent. has an extinction coefficient of 18 on the curve, or by calculation, 690×0·01+11×0·99=17·8.

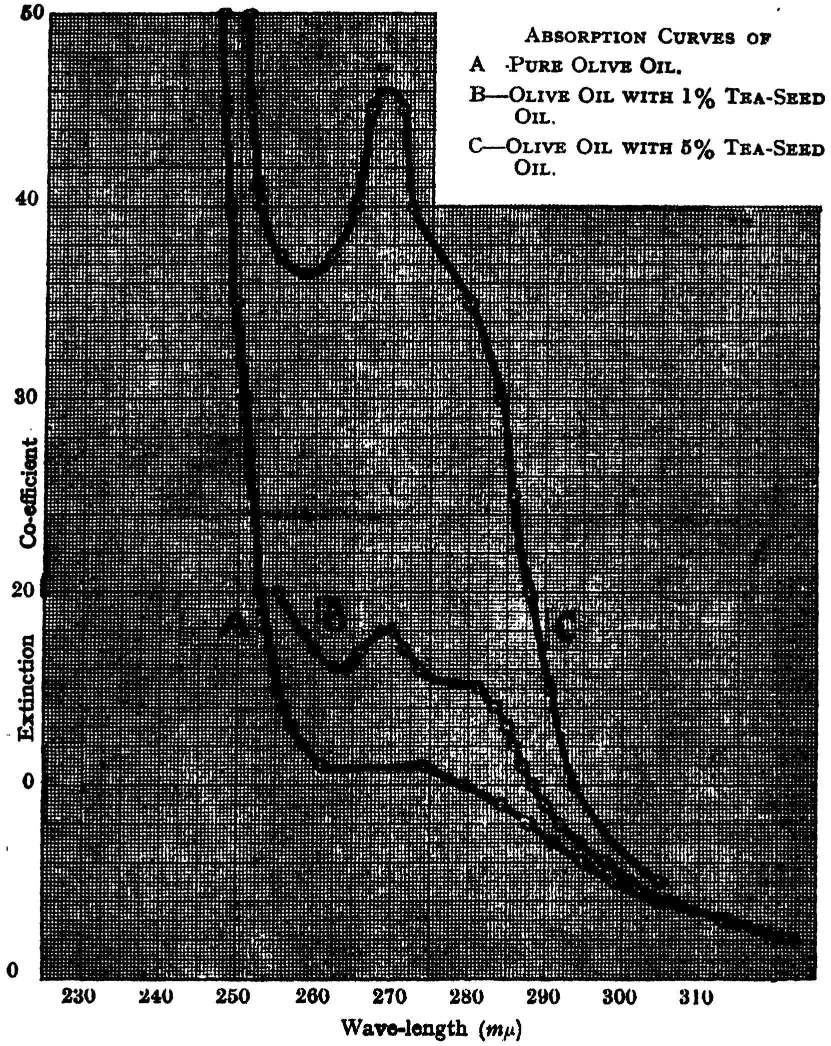

Fig. II

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THE USE OF THE SPECTROGRAPH IN METALLURGICAL ANALYSIS

BY D. M. SMITH, A.R.C.S., B.SC., D.I.C.

INTRODUCTORY.—During the last ten years or so increasing use has been made of spectrographic methods in analytical laboratories, not only as a check on chemical control of material, but also for routine testing. With a view to encouraging the wider adoption of these methods by metallurgists, systematic investigation of the subject has been in progress by the British Non-Ferrous Metals Research Association for some years. This work has been largely concerned with testing the application of these methods to the determination of impurities in metals of commercial importance, by means of a simple and inexpensive technique and equipment. It is the purpose of this contribution to describe briefly what is being done in this direction, and to indicate possible future developments with a view to improving the reliability and accuracy of spectrographic analysis and to extending its scope of application.

TECHNIQUE.—For the analysis of metals and alloys, the quartz spectrograph is generally used, qualitative and quantitative analysis being carried out by observation of the characteristic lines in ordinary photographic records of arc- and spark-spectra. Mr. Twyman has dealt, in ample detail, with the apparatus used in this work, and there is no need, therefore, to enlarge on that part of the subject.

As the amount of an impurity or alloying constituent increases, its characteristic lines show a corresponding increase in intensity, and the general principle of spectrum analysis consists of the correlation of the intensities of these lines with the amounts of the constituents giving rise to them.*

While not wishing to detract from the value of purely visual methods of analysis (*cf.* F. Twyman[1]), I would point out that there are several important advantages of photographed spectra. Apart from the value of having a permanent record of each analysis, the most sensitive lines used in analytical work are to be found, in the main, in the ultra-violet part of the spectrum, and the most satisfactory method of examining this region is by means of photographic records. Moreover, since quantitative determinations are based on comparisons of the intensities of lines (as represented by the densities of their images on the photographic plate) the absence of colour is much to be preferred.

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* An illustration was shown of the arc-spectra of the following grades of zinc:—spectroscopically pure; chemically pure; electrolytic; common spelter.
A simple means of rapidly identifying such material is thus obtained.
(The slides shown at the meeting were actual spectra obtained with a small-size spectrograph. In this way the inevitable loss of detail by reproduction was avoided).

With regard to the form of the samples, the arc or spark between metallic electrodes, consisting of pieces of the sample under test, has much to commend it from the point of view of convenience in operation. Preliminary treatment, as required in chemical analysis, such as dissolving the metal and subsequently precipitating, is avoided. It is not always possible or convenient to prepare electrodes in a suitable form for an arc to be obtained in this way, and more use is now being made of the arc between pure graphite electrodes. The arc is more sensitive than the spark for the detection of traces of certain impurities, and since it is very difficult to obtain metallic arcs with tin and lead, graphite electrodes have distinct advantages for such metals. In the analysis of small copper samples Milbourn employs a similar technique, but with the small modification of using a pure copper rod in place of the upper graphite electrode.

STANDARD ALLOYS.—Before it is possible to standardise a spectrographic method of analysis of any given metal or alloy, considerable attention must be given to the question of the reliability of the standard alloys, since the method is based on the quantitative interpretation of the spectra of alloys of accurately known composition.*

The most obvious method of controlling the standard alloys is to rely upon the results of careful chemical analyses, checked and confirmed by the independent work of skilled analysts, and in many cases this is the only method available. For metals of low m.p., such as lead, tin, and zinc, however, the melting, mixing and casting of accurately weighed constituents *in vacuo* has proved a very satisfactory method of producing alloys of definite composition. This method of preparation fails in cases where the alloying constituents tend to separate out on cooling. It is often difficult, for example, to obtain in this way homogeneous alloys containing even small quantities of lead.

A method recently found useful for checking the reliability of chemically analysed samples proposed as standards for spectrographic work, involves the use of "synthetic spectra." The spectrum of a standard alloy containing the highest content of the series (which is easier to check by chemical analysis than a sample containing only a trace) is superimposed on that of the pure metal forming the main constituent, the times of exposure being systematically varied.†

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* The arc-spectra of synthetic alloys of zinc with 0·75, 0·25, 0·1, 0·01, and 0·001 per cent. of cadmium were shown as an illustration of quantitative standard spectra.

† Two slides illustrating the principle of this method were shown. The two components of each synthetic spectrum were photographed separately and in juxtaposition in the first slide, the upper spectrum in each case being that of the standard lead alloy (lead containing 0·5 per cent. of tin) and the lower spectrum that of pure lead. The corresponding times of exposure were as follows:

Lead + 0·5 per cent. of tin:	5; 10; 15; 30; 45 seconds.
Pure lead:	55; 50; 45; 30; 15 ,,

By superposing the spectra in each pair, as shown in the second slide, a series of five spectra was obtained, in which the tin lines showed a systematic increase in intensity, the lines due to the primary constituent (lead) remaining of constant intensity.

A curve can then be constructed showing the relation between the percentage of impurity present and the time of exposure of the standard alloy which gives a spectrum identical with that of the sample under examination. Irregularities are then readily detected from the position of individual points with regard to the mean curve. This method has been applied to the determination of small quantities of bismuth in copper,[2] and it shows promise of fairly wide applicability.

METHODS OF ANALYSIS.—*The Necessity for Standardisation of Technique.*—Whether the arc or spark be used as the source of the spectrum, there are a number of variables which require rigid control to secure reproducibility of the spectra. The aim has been so to choose the technique in individual applications as to be able to obtain from the spectrum of the sample itself all the quantitative information required. At the same time it should be pointed out that the method of comparing the spectrum of a sample with those of selected standard alloys (generally referred to as the "comparison sample" method) has been found extremely useful, and is still very largely used, particularly in testing whether a material conforms to specification.

Quantitative Interpretation of the Spectra.—The general applicability of spectrographic methods in different laboratories, under somewhat different conditions, has also received attention, and, wherever possible, the conditions for the production of the spectra have been standardised from this point of view.

The basic principle underlying practically all the methods now in use for quantitative analysis was first described by W. Gerlach[3] in 1925, and is known as the "internal standard" method. Equality of intensity between an impurity line and a line of the main constituent is correlated with the percentage of impurity present. If sufficient pairs of lines of this kind are available, analysis is possible in fairly close steps.

In a large number of cases sufficient lines suitable as internal standards are not available, and, in order to distinguish between more closely-graded percentages, methods using auxiliary spectra "coupled" with those of the samples under examination have been used, as, for example, the tin spectrum, which gives a fairly wide range of lines of different intensity. Owing to the different characters of a number of spectrum lines, the use of an auxiliary *alloy* has been found to give more suitable lines as intensity standards, such as, *e.g.* an alloy of copper with 1 per cent. of tin for the analysis of copper samples. Similarly, an auxiliary alloy of lead with 0·4 per cent. of tin can be used for the analysis of lead samples.[4] Here one is comparing impurity lines with tin lines in the auxiliary spectrum—a procedure which appears more satisfactory, since both types of lines are intrinsically the same.*

In order to increase the accuracy of analysis, methods based on the above principles, but also giving the possibility of assigning numerical values to the intensities of the lines, have been devised. The recording or non-recording microphotometers and the logarithmic sector-wedge methods may be quoted as examples.*

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* Arc-spectra of alloys of copper with various quantities of manganese afforded an illustration of the internal standard method. The superposition of a tin spectrum and the juxtaposition of a spectrum of copper with 1 per cent. of tin was shown in the case of a number of copper-alloy spectra.

Metallurgical Applications.—Considerable progress has been made in the delicacy of the chemical detection of traces of elements, so that the superiority of spectrographic methods in this respect is not quite so pronounced as formerly. On the other hand, the chemical determination of traces of impurities is usually laborious, involving tedious separations from a large bulk of material, and requiring considerable skill. It is, moreover, in the region of traces of impurities that the spectrograph is shown to its best advantage, and about 1 per cent. may be taken as the upper practical limit of its present sphere of usefulness. In this particular field, standardised methods have been developed by the British Non-Ferrous Metals Research Association for the determination of the usual impurities in zinc, copper, tin, lead and aluminium, and work is now proceeding on the determination of the impurities commonly occurring in nickel.

An excellent example of the value of spectrographic methods is afforded by the analysis of "chemical lead." It is possible to determine the copper, silver, bismuth, antimony, zinc, and cadmium contents of this material with sufficient certainty to determine whether it conforms or not to specification. The determination of traces of bismuth in copper and traces of cadmium in zinc are further examples of metallurgical importance. Such analyses as these can be carried out as a matter of routine with great saving of time.

Many other interesting applications might easily be enumerated, of which the following are typical:—

1. *Testing material for segregation, or non-homogeneous distribution of impurities and alloying constituents.*—The fact that in spectrum analysis only a very small amount of the material takes part in the discharge, becomes an advantage in this case.

2. *The analysis (for metallic constituents) of coatings, dross, inclusions and the like.*—In cases such as these it is generally only possible to give little more than a qualitative analysis, but with experience it is possible to distinguish between the major constituents and those occurring in very small quantities.

3. *The analysis of samples too small for chemical analysis.*—The spectrographic method gives a complete qualitative, if not quantitative, analysis of the material.

4. *Identification of material.*—In addition to the rapid testing of samples of unknown composition, cases are known where it has been possible to identify or indicate the source of supply or the process of refining employed by the presence of traces of residual metallic constituents (of deoxidisers for example).

A large amount of valuable work has been carried out in recent years in other quarters, and the laboratory of Messrs. I.C.I. Metals, Ltd., may be specially mentioned in this connection. Papers giving details of standardised methods for the analysis of lead, brass and copper have been published by Brownsdon, and by van Someren[5] and Milbourn.[6] The work for the British Non-Ferrous Metals Association has been considerably assisted by this and other parallel work which has been made available.

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* Logarithmic sector-wedge spectrograms were shown of lead-tin alloys, containing up to 3 per cent. of tin, the lengths of the tin lines increasing with increasing percentage and the lead lines remaining of fairly constant length in the different spectra.

In Germany numerous publications have appeared under the authorship of Gerlach and Scheibe[7] and their colleagues, and in Belgium, Breckpot[8] has recently published an account of his extensive study of the analysis of copper. Increasing attention is also being given to spectrographic methods in America, and since the middle of 1933 about fifty publications (from various countries, including our own) of metallurgical interest have appeared.

PRESENT TENDENCIES AND FUTURE DEVELOPMENTS.—Owing to the increasing and widening application of spectrographic methods, several different aspects of the subject have been investigated, some in considerable detail. Generally speaking, the different lines of attack both in England and abroad have been, and still are, in the following three directions:

(i) Towards greater stability and reproducibility of arc and spark discharges, with a view to obtaining improved regularity in the results. Valves and undamped high-frequency oscillations[9] have been used for spark circuits, for example, and the intermittent arc[10] method has been proposed for rapidly oxidisable metals, such as aluminium.

(ii) Improvements in methods of "sampling" (the word sampling in this connection being taken to mean the selection of samples to be subjected to spectrographic examination), in order to extend the application of the spectrograph in quantitative analysis and to increase the reliability of the results.

Solution and "pastille" methods,[11] oxide and sulphate powder samples have been proposed with this end in view, and the method described and so successfully used by Judd Lewis may be instanced in this connection.

(iii) Increase in sensitivity of detection of traces and in the accuracy of determination. The use of higher currents in the arc, for example, has yielded increased sensitivity in the detection of traces of bismuth, and electrolytic deposition and preliminary chemical separation have given a similar increase in sensitivity.

The use of photometric devices to obtain increased accuracy is also being investigated. It may be observed, however, that there is a danger, when introducing too many refinements, that the simplicity and speed of spectrum analysis, wherein lie its chief attractions, may be lost to a considerable extent. With simplification of photometric methods and the possibility of reducing the personal factor, there is no doubt that such methods will be increasingly used.

An attempt has been made to cover a wide field, although restricted to metallurgical analysis, and more particularly to the investigations on non-ferrous metals and alloys, which have now been proceeding for nearly ten years and are still in progress for the British Non-Ferrous Metals Research Association. It is hoped, however, that this contribution will have been of some general analytical interest.

I wish to thank the Society of Public Analysts for the invitation to take part in the Symposium and the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish this contribution.

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DISCUSSION

Mr. J. H. GARDINER, referring to the use of the spectroscope in criminology, mentioned that more than sixty years ago Dr. Meymott Tidy, who was then Professor of Medical Jurisprudence at the London Hospital, showed at the Royal Institution the absorption bands of blood that he had extracted from the hat of a suspected criminal; this formed a link in the evidence leading to the conviction of a man named Müller, who "murdered Mr. Briggs on a railway train."

He (Mr. Gardiner) had the honour of working under the late Sir William Crookes from 1881 until his death in 1919, and during all that time the spectroscope was in constant use for the researches carried out in the laboratory. One lengthy work was the spectroscopic examination of some twenty earthy meteorites obtained from the collection in the British Museum, the lines between $m\mu$ 400 and 240 of all the elements present being identified. The method used (for they were all non-conductors of electricity) was to mix the finely powdered aerolite with pure precipitated silver, and by means of a hydraulic press to form the material into blocks from which electrodes could be cut; from the resulting arc-spectra the lines due to the silver could easily be recognised and those due to the aerolite observed. For a particular research it was desired to obtain some absolutely pure iron, but it proved extremely difficult, in fact impossible, to get. Help was given by many metallurgists, and the purest specimen was one from the Bureau of Standards, Washington, but even in this faint traces of the manganese lines were shown. The last work upon which Sir William was engaged was the separation of the element scandium from the rare mineral wiikite; on account of the rarity of the substance the arc-spectrum method could not be followed, and the chemical work of the separation was directed by constant reference to the spark spectrum of a solution of the nitrate. The most difficult step in the work was the removal of traces of holmium that accompanied the scandium in the mineral, and Mr. Gardiner exhibited the first spectrum photograph, which showed that this substance had been successfully removed and "Scandium Purissimum" obtained. Photographs, signed by Sir William, of cathode luminescence spectra of some rare earths of the yttria series, were also exhibited; in these photographs bands were observed that were thought to be due to a novel element which was provisionally named "victorium," but, unfortunately, the work was never completed.

Mr. M. Milbourn said that he was using spectrographic methods in an industrial laboratory, where they had proved themselves indispensable. Without minimising the value of quantitative work, it would be well to bear in mind that much could be done without making any actual quantitative estimate. For instance, the purity of chemical precipitates could be checked; or one could readily determine whether the metallic constituents of two samples, supposed to be similar, were really identical; or again, when two samples were behaving differently, differences in composition, particularly with regard to the minor constituents, could be rapidly ascertained. In quantitative work, more particularly in routine analyses to specification, some measure of accuracy could be sacrificed to speed, any doubtful results being checked by chemical methods. Close collaboration in the use of chemical and spectrographic analysis ensured that one method acted as a constant check upon the other. Sometimes spectrographic methods were definitely superior to chemical methods, as in the determination of minute quantities of magnesium.

The President, in proposing a hearty vote of thanks to all the speakers for their contribution to the symposium, asked the members to include in their thanks Messrs. Adam Hilger, Ltd., for the special display of spectroscopic instruments.

Occurrence of an Unsaturated Hydrocarbon in Olive Oil

By T. THORBJARNARSON and J. C. DRUMMOND, D.Sc., F.I.C.

In the course of an investigation with the object of distinguishing olive oil from other oils, Bolton and Williams[1] came to the conclusion that the natural oils and fats could be classed in four groups according to the degree of unsaturation of their unsaponifiable matter. Olive oil was peculiar in being characterised by unsaponifiable matter with high iodine value (197 to 204).

So far as we are aware, there is only one subsequent investigation recorded in the literature which throws light on this peculiarity. Sani[2] separated an unsaturated hydrocarbon from the non-saponifiable fraction of olive oil by distillation at reduced pressure. The elementary analyses and determination of molecular weight led him to suggest the formula $C_{21}H_{36}$ for the compound, but he does not appear to have determined its iodine value. His examination of this compound was cursory and suggested the importance of making a more thorough investigation of its nature.

The olive oil employed for the main part of the experiment was an authentic product of Palestinian origin.* It had the following characteristics:

Saponification value, 191; iodine value, 82·6; $n_D^{18°}$, 1·4707; unsaponifiable matter, 1·12 per cent.; iodine value of unsaponifiable matter, 255; mean equivalent of fatty acids, 279; iodine value of fatty acids, 85·3.

Preparation of Unsaponifiable Matter.—The olive oil was saponified by 30 minutes' treatment with an excess of hot alcoholic potassium hydroxide solution.

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* We are greatly indebted to Mr. E. R. Bolton, F.I.C., for his help in obtaining this and other representative oils examined during the course of this investigation.

The soap solution was diluted with three volumes of water and repeatedly extracted with redistilled ether. After the ethereal extract had been washed and the solvent distilled off, the residue was re-saponified with sodium ethoxide, and the extraction process was repeated. The final yield of unsaponifiable matter from 1 kg. of oil was 9·6 g.

This material was a soft, yellow wax with iodine value 255, and contained 16·9 per cent. of material (sterol) precipitated by digitonin. An attempt was made to separate the constituents of the unsaponifiable matter by fractional crystallisation from hot methyl alcohol. For this purpose 7 g. were treated with 500 ml. of hot methyl alcohol. A small amount of the substance would not dissolve in spite of continued heating. This insoluble material was filtered off and dried. It was a dark-brown, semi-solid oil (substance A) with iodine value 130. The filtrate was concentrated to half its volume and kept at 0° C. A crystalline substance of a faint yellow colour separated (substance B). It was filtered off, and the filtrate was concentrated to half its volume once more and stored at 0° C. A crystalline substance separated from the concentrated filtrate, along with some oily droplets. This fraction was isolated and again taken up in a small amount of methyl alcohol, the crystalline substance (C) being less soluble than the oil.

The material soluble in the methyl alcohol was obtained by removal of the solvent. It was a heavy colourless oil (D) which, on cooling and standing, deposited a small amount of a soft waxy crystalline material. This treatment with methyl alcohol effected a considerable concentration in the more soluble fractions of the material with high iodine value.

	Iodine value
Original non-saponifiable matter	255
Fraction (A)	130
Fraction (B)	108
Fraction (C)	181
Fraction (D)	342

These fractions were examined chemically, with the result that A and B were found to consist largely of crude "sitosterol." Further examination of these "sterol" fractions and those obtained in the adsorption experiments later to be described showed that they consisted mainly of sitosterol accompanied by the usual small proportions of dihydrositosterol, ergosterol and dihydroergosterol. Fraction D contained a large proportion of a hydrocarbon which, to our surprise, appeared to resemble squalene.

Naturally, our main interest was centred on the last-mentioned fraction, but efforts to free it completely from oxygen-containing substances by the use of solvents were not successful. It was decided, therefore, to try selective adsorption as a means of separating the hydrocarbon more satisfactorily.

A preparation of the unsaponifiable matter was dissolved in a small quantity of a mixture of 90 per cent. of petroleum spirit (b.p. 40–60° C.) and 10 per cent. of benzene and passed slowly through a column of Merck's specially-prepared aluminium oxide. Four coloured zones appeared and gradually moved down the column during washing with the same solvent mixture. The washing was continued until the lowest of the coloured zones had almost reached the bottom of the column. The aluminium oxide column was then divided into portions corresponding with the zones. Each fraction of the aluminium oxide was eluted by washing with a mixture of 75 per cent. of petroleum spirit and 25 per cent. of methyl alcohol. The iodine values of the various fractions were determined, and their spectroscopic properties were examined for us by Dr. R. J. Macwalter, to whom we desire to express our thanks.

TABLE I

2·05 g. OF UNSAPONIFIABLE MATTER ADSORBED

	Weight g.	Iodine value	Absorption bands $m\mu$*
Original unsaponifiable matter	2·05	255	307 W 297 W General absorption
Filtrate material not adsorbed	1·23	345	352 W 333 S+ 324 S+ 301 S+ 286 S+ 275 M
Bottom band of column. Least readily adsorbed.	0·03	209	349 W 326 W 295 W 282 W 270 M 260 M
2nd zone from bottom of column.	0·02	190	303 W 289 W 277 edge
3rd zone from bottom.	0·34	130	Moderate general absorption
Top zone of column. Most strongly adsorbed.	0·43	104	294 M 281 M 261 V.W.

* W signifies weak band; M signifies band of moderate intensity; S signifies well-defined absorption.

The spectroscopic examination of the fractions revealed interesting information. The bands exhibited by the adsorbed material from the top of the column indicated clearly the presence of ergosterol. They were also seen sharply when the material from the next zone (3rd) was recrystallised from methyl alcohol, but were masked in the examination of the crude fraction by general absorption, due in large part to the presence of a pigment of the xanthophyll type. The spectroscopic properties of the hydrocarbon fraction will be referred to again later.

The fraction of the unsaponifiable matter which passed unadsorbed through the column was a colourless and odourless mobile oil. From it there appeared, on standing in a cool place, a small amount of a crystalline waxy substance which was readily separated, and which, after one recrystallisation from methyl alcohol, showed no absorption of iodine and melted indefinitely at 68°. On analysis it gave the following results:—*Carbon, 84·10; hydrogen, 14·77 per cent. (4·714 mg. gave 14·35 mg. of carbon dioxide and 6.22 mg. of water). This analytical result, together with the properties of the material, strongly suggest that it is a mixture of saturated, aliphatic hydrocarbons similar to the preparations isolated by Chibnall and his colleagues from a variety of plant materials (*e.g.* a mixture of C_{29} H_{60} and $C_{31}H_{62}$, m.p. 63–4° C., isolated by Chibnall and Sahai[3] from the wax of brussels sprouts). The amount of the saturated hydrocarbon preparation was insufficient to provide for a more thorough examination.

A sample of the liquid fraction which remained behind after the solid hydrocarbon had been removed was analysed. The results indicated that a great part consisted of an unsaturated hydrocarbon, possibly of the squalene type, but that very small traces of other substances, some of which contained oxygen, were also present. Bromination in anhydrous ether solution or treatment with hydrochloric acid gas in dry acetone gave crystalline derivatives which bore a superficial resemblance to the dodecabromide and hexahydrochloride, respectively, of squalene. It has been found impossible satisfactorily to free the unsaturated hydrocarbon from the saturated hydrocarbons and other substances by distillation under reduced pressure.

After removal of the saturated component as described above, distillation at low pressure effects a satisfactory purification of the unsaturated hydrocarbon. In the fractionation of 4 g. at a pressure of 0·08 mm. most of the liquid passed over in the range 170° C. to 190° C., and a considerable proportion of this was collected between 187° and 190° C.

The distillation effected considerable purification of the hydrocarbon, as judged not only by the analytical results, but also by the spectroscopic examination. The crude hydrocarbon fraction, as reference to Table I will show, exhibited a number of absorption bands. The nature of the substance responsible for these has not been determined, but it is of interest to note that the group of bands recorded here has also been detected in this laboratory in the corresponding fraction from wheat-germ oil. The band at 275*mμ* may possibly be referred to carotene, but the others are more probably related to a cyclic unsaturated hydrocarbon. Further work on this question is in progress. The distilled hydrocarbon showed a much simpler picture, as only three poorly-defined bands, at 324, 292 and 281*mμ*, were detected. So far as we have been able to determine, these bands are due to minute traces of impurity. They are not, we believe, related to the main hydrocarbon constituent. The distilled fraction was a clear, colourless mobile fluid. On analysis it gave the figures: Carbon, 87·53, 87·71; hydrogen, 12·62, 12·44 per cent. (calculated for $C_{30}H_{50}$, C=87·70; H=12·30 per cent.). It is interesting to note that the analytical data recorded by Sani are in agreement with these figures (C=87·45, 87·79; H=12·20, 11·80 per cent.). He undoubtedly isolated almost pure squalene, but was misled by a low figure for his molecular weight determination. He noted absorption of halogens, but did not observe the formation of crystalline derivatives.

Hydrochloride.—In dry acetone saturated with hydrochloric acid gas the distilled hydrocarbon gave a good yield of a crystalline derivative. The crude hydrochloride melted rather indefinitely between 112° and 120° C., recalling the similar behaviour of squalene hydrochloride, as described by several authorities. This compound was found to contain 33·61 per cent. of chlorine (calculated for $C_{30}H_{56}Cl_6$ = 33·86 per cent.). It was purified by fractional crystallisation from acetone after the manner described by Heilbron, Kamm and Morton[4] in their studies of the squalene hydrochlorides. The less soluble fractions gave rise to a material of a high m.p. (148–9° C.), which did not change its character on subsequent treatments with the solvent. In a recent experiment one fraction melting as high as 150° C. was obtained.* The main part of the more soluble portion gave a well-defined product melting unsatisfactorily between 118° C. and 124° C., but small amounts of preparations melting as low as 109° to 111° C., and even 100° to 101° C. were obtained from mother liquors. The results of this fractionation resemble those obtained when squalene hydrochloride is similarly treated (André and Canal,[5] Heilbron *et al.*[4]).

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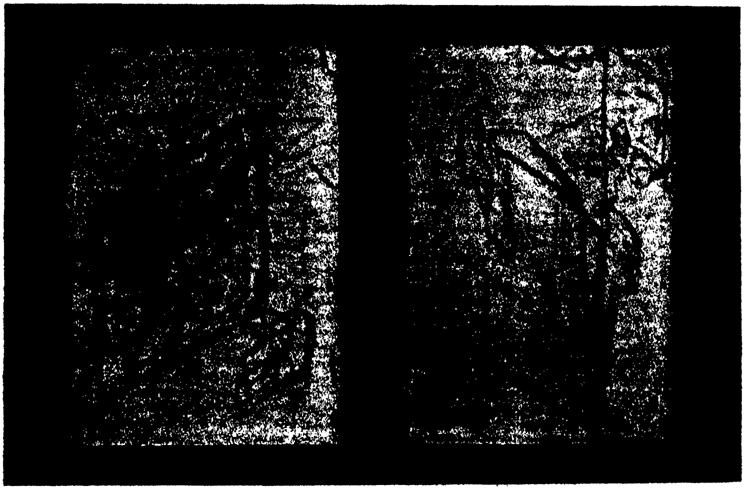
* Elementary analyses recorded in this paper were carried out by Dr. Ing. Schoeller of Berlin and by Dr. G. Weiler of Oxford.

The analysis of the two main fractions gave the following figures:

Hydrochloride m.p. 148–9° C. Chlorine 33·14 per cent.
„ „ 100–1° C. „ 33·54 „

Fig. 1 shows the crystalline form of the hydrochloride (m.p. 110–116° C.), and that of squalene isolated from the liver oil of *Scymnorrhinus lichia.*



a. Hydrochloride from hydrocarbon derived from olive oil. *b.* Squalene hydrochloride.

Bromide.—The hydrocarbon dissolved in anhydrous ether and treated with an excess of bromine at −25° C. deposited a white micro-crystalline product superficially resembling the dodecabromide of squalene. The separated bromide darkened at 150° C. and melted, with signs of decomposition, at 187–189° C. The percentage of bromine found on analysis was 69·7. (Calculated for $C_{30}H_{50}Br_{12}$; Br = 69·7 per cent.)

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* There would appear to be need for a re-investigation of the isomeric hydrochlorides of squalene. Fractionation of the crude hydrochloride may yield a wide range of crystalline products with different melting-points. Other workers have also noted this peculiarity.

PREPARATION OF HYDROCHLORIDE DIRECT FROM OLIVE OIL.—It being apparent, from the iodine value of the unsaponifiable matter and also from the actual yield of the hydrocarbon, that the latter was present in this sample of olive oil to the extent of approximately 0·5 per cent., it seemed of interest to attempt the preparation of the hydrochloride directly from the oil itself. Actually, the attempt was successful, in that characteristic crystals of this derivative separated out when the acetone solution of the oil was subjected to treatment with dry hydrochloric acid gas. The yield was, however, less than one-third of what might have been expected, and the experiment, considered as an analytical test for olive oil, was unsatisfactory, because of the separation of layers and the production of a large amount of dark brown, pigmented material. When heated, the hydrochloride thus produced, and purified by washing with anhydrous ether, showed shrinkage at 110° C., and finally melted rather indefinitely between 120° and 129° C. The chlorine-content was 33·22 per cent.

PROPORTION OF THE HYDROCARBON IN OLIVE OILS OF DIFFERENT ORIGIN.—A number of genuine olive oils of known origin, and one authentic sample of tea-seed oil, were examined for the presence of the hydrocarbon. The oils were saponified as described earlier in the paper, and the iodine values of the unsaponifiable matter were determined. The unsaponifiable fractions were then dissolved in a mixture of 75 per cent. of light petroleum spirit and 25 per cent. of benzene, and passed through a column of adsorbent aluminium oxide. The columns were washed through with a solvent mixture of similar proportions, and the materials which passed through without being adsorbed were recovered. The iodine values of these were determined.

It will be seen from the following table that all the samples of olive oil gave fractions which passed through the adsorption column, and which consisted almost entirely of the hydrocarbon. The presence of the hydrocarbon was in each case confirmed by the preparation of the crystalline hydrochloride. The results of the examination of the sample of tea-seed oil gave no evidence that squalene or any similar compound was present.

TABLE II

Oil	Iodine value of unsaponifiable matter	"Hydrocarbon" in unsaponifiable matter Per Cent.	Iodine value of "hydrocarbon" fraction
Palestine	255	64	345
Tunisian	194	38	360
Spanish (Aragon) ..	203	31	374
Turkish	263	58	364
Italian	235	—	—
Tea-seed	157	7*	130

* In view of the low iodine value of the hydrocarbon fraction from tea-seed oil, it is improbable that any significant amount of squalene is present.

COMPARISON OF PROPERTIES OF OLIVE-OIL HYDROCARBON AND SQUALENE

	Recorded data for squalene $C_{30}H_{50}$	Hydrocarbon from olive oil
Composition	C = 87·8 per cent.	C = 87·71, 87·53 per cent.
	H = 12·2 ,,	H = 12·62, 12·44 ,,
B.p.	235–7° C. (0·15 mm.) (*a*)	187–190° C. (0·08 mm.)
Refractive index, $n_D^{20°}$	1·4965–7 (*a, b, c, d*)	1·4964
Iodine value	367·9 (*b*), 377·6 (*d*)	372
Mol.wt. cryoscopic (benzene)	394·391 (*b*), 391 (*d*)	368
Hydrochlorides	m.p. 144–5° C., Cl = 33·9 per cent.	m.p. 148–9° C., Cl = 33·84 per cent.
	m.p. 107–8° C., Cl = 35·3 ,, (*e*)	m.p. 109–11° C.,
	m.p. 144–5° C., Cl = 33·2	m.p. 100–1° C., Cl = 33·5 per cent.
	m.p. 107–8° C., Cl = 33·9	
	m.p. 144–5° C., Cl = 33·7	
	m.p. 113–4° C., Cl = 33·85 (*d*)	
	m.p. 107–8° C., Cl = 33·6	
Dodecabromide	darkens at 160° C., melts with decomposition at 185° C.	darkens at 150° C., melts with decomposition at 187° C.
	Br = 69·7 per cent. (*b*)	Br = 69·7 per cent.

(*a*) Majima and Kubota, *Jap. J. Chem.*, 1922, **1**, 9.
(*b*) Chapman, *J. Chem. Soc.*, 1917, 56; 1918, 458.
(*c*) Tsujimoto, *J. Chem. Ind. Tokio*, 1906, **9**, 953; *J. Ind. Eng. Chem.*, 1916, **8**, 889; 1920, **12**, 63.
(*d*) Heilbron, Kamm and Morton, *J. Chem. Soc.*, 1926, 1630.
(*e*) André and Canal, *Compt. rend.*, 1925, **181**, 612.

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UNIVERSITY COLLEGE
UNIVERSITY OF LONDON

The Determination of small Quantities of Chlorine in Commercial Benzaldehyde

BY C. G. DAUBNEY, M.SC., A.I.C.

THERE are two main types of method available for determining the chlorine-content of commercial benzaldehyde, which is often of the order of 0·01 per cent.:—(i) Wet-oxidation methods, involving the use of mixtures of sulphuric and nitric acids. (ii) Methods in which the benzaldehyde is burnt in a lamp, and the products of combustion are examined for chlorine.

(i) Salamon,[1] and later, Faust and Spangler,[2] advocate treating a known weight of benzaldehyde with a mixture of concentrated sulphuric and nitric acids, distilling the mixture, and collecting the evolved vapours in silver nitrate solution. Methods of this kind have been investigated very fully by the firm of Schimmel,[3] who raise the objection that, by this procedure, chlorine which may be in the benzene nucleus is not necessarily liberated.

Other objections might be urged, such as the inherent disadvantage of using strong acids which produce a violent reaction, the difficulty of scrubbing the rapidly evolved gases, and the necessarily large volume of scrubbing liquid in which to determine a small quantity of chlorine.

(ii) Schimmel & Co.[3] advocate the use of a burning method. This consists in burning a quantity of benzaldehyde in a suitable lamp, scrubbing the products of combustion in towers containing $N/50$ sodium hydroxide solution, and converting the resulting sodium chloride into silver chloride.

To this process, also, objections can be raised: the chlorine may react with the sodium hydroxide to form chlorate or hypochlorite, and a large volume of chlorine-free scrubbing liquid is required.

The modified method adopted in the present investigation is as follows:

Benzaldehyde is burnt in a Richardson lamp[4] in a current of air previously freed from chlorine by passage over heated silver gauze, A, and the products of combustion are passed over a second piece of hot silver gauze, B. The chlorine present is converted into silver chloride, which is subsequently extracted with ammonia (sp.gr. 0·880), re-precipitated, and collected for weighing. The method has the advantage that the final aqueous liquid from which the silver chloride is precipitated is of small bulk.

The determination can proceed as long as is necessary to give a weighable quantity of silver chloride, and the one precaution to observe is the prevention of a sooty flame.

DETAILS OF METHOD.—The two rolls of silver gauze, A and B, are first cleaned by immersion in ammonia solution (sp.gr. 0·880), washed with water, dried and gently heated in a flame. They are then slid into silica tubes (in which they fit tightly), being followed by asbestos plugs and, finally, by rubber stoppers.

The lamp is filled with benzaldehyde, the wick (not glass capillaries) is adjusted to give a small flame, and the whole is weighed. The rest of the Richardson apparatus is connected (without the usual absorption tube) with the silica tubes placed side-by-side in iron-gauze shields. These tubes are heated to dull redness before the apparatus is connected with the suction pump.

The lighted lamp is then slid into position, the air-flow is adjusted to give a small non-smoky flame, and the shield is slipped down on to the mercury seal. The benzaldehyde is thus burning in a chlorine-free stream of air, and the products of combustion are freed from chlorine by the hot silver gauze, B.

When sufficient benzaldehyde has been burnt—this depending upon the expected chlorine-content—the lamp is removed and re-weighed. When cool, the tube with gauze, B, is disconnected, the ends, inside and outside, are cleaned, and, without removal of the gauze, placed in a test-tube. Three successive portions of 1·5 ml. of ammonia (sp.gr. 0·880) are dropped on to the gauze, and after this has been left for 10 minutes some 5 ml. of water are used for washing the gauze and tube. The dilute ammonia solution is then acidified with a minimum quantity of nitric acid, a few drops of silver nitrate solution are added, and the precipitated silver chloride is left to settle. Coagulation is assisted by the addition of a few drops of ether.

The silver chloride is collected in a Gooch crucible, washed first with $N/100$

nitric acid and then with absolute alcohol, dried at 125° C., cooled and weighed. It is then dissolved in ammonia, and the crucible is re-weighed. Usually a few tenths of a milligram of carbon remain undissolved.

The following table shows the results obtained both with commercial samples of benzaldehyde and with genuine natural oil of bitter almonds. Check determinations in which known quantities of chlorine were added to the almost chlorine-free oil of bitter almonds, indicate the reliability of the method.

Description of sample	Weight of substance burnt g.	Silver chloride g.	Chlorine Per Cent.
Oil of bitter almonds, Sample A	5·58	Opalescence	Trace
„ „ „ „ „ B	10·31	0·0006	0·0014
„ „ „ „ „ C	9·88	0·0006	0·0015
„ „ „ „ „ D	12·71	0·0003	0·0006
Oil of bitter almonds			
+0·013 per cent. Cl as *o*-chlorobenzaldehyde	7·39	0·0041	0·014
+0·025 „ „ Cl „ „	3·13	0·0033	0·026
+0·074 „ „ Cl „ „	1·56	0·0047	0·075
+0·131 „ „ Cl as *p*-chlorotoluene + benzyl chloride	1·32	0·0071	0·133
+0·022 „ „ Cl as „ „	2·18	0·0019	0·022
Commercial benzaldehyde. Sample E ..	1·92	0·0016	0·021
	4·59	0·0042	0·023
	5·59	0·0045	0·020
Commercial benzaldehyde (chlorine-free). Sample F	2·93	0·0009	0·008
	5·87	0·0018	0·008
	7·44	0·0023	0·007
Commercial benzaldehyde. Sample G ..	4·38	0·0010	0·006
„ H ..	5·32	0·0022	0·010
	4·86	0·0057	0·029
	5·05	0·0055	0·027
"Technical" K ..	1·500	0·0239	0·39
	1·201	0·0197	0·40

SUMMARY.—(i) A method is described for the determination of total chlorine in commercial benzaldehyde and oil of bitter almonds.

(ii) Oil of bitter almonds is shown to contain about 0·001 per cent. of chlorine.

(iii) Known amounts of chlorine in the form of organic chlorine compounds added to oil of bitter almonds are recoverable.

(iv) Commercial benzaldehydes contain between 0·005 and 0·03 per cent. of chlorine. One sample of technical benzaldehyde contained 0·40 per cent. of chlorine.

I wish to thank the Government Chemist for permission to publish this paper, and Mr. S. F. Holder, B.Sc., for assistance with the analytical work.

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STRAND, W.C.2

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2. M. Spangler, *Chem.-Ztg.*, 1925, 49, 724.
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4. *J. Inst. Petr. Tech.*, 1921, 7, 26.

Erratum.—"Lead in Biological Materials, with Special Reference to Bone," by Roche Lynch, Slater and Osler.

The authors regret an unfortunate error in their paper on pages 801–2 of the December issue. The sentence beginning in the last line of p. 801 should read as follows:—"If we take, for example, a 12-stone man who has 100 p.p.m. of lead in his bones, he will have in his whole skeleton 1·5 grms. (23 grains) of lead (as Pb), or 2·0 grms. (31 grains) of lead phosphate, $Pb_3(PO_4)_2$."

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

SOME EXAMPLES OF FLUORESCENCE ACIDIMETRIC AND ADSORPTION INDICATORS

Volumetric determinations in ultra-violet light have been confined, up to the present, to acidimetric titrations, *e.g.* with quinine sulphate (Mellet and Bischoff, *Compt. rend.*, 1926, **182**, 1616) or umbelliferone (Robl, *Ber.*, 1926, **59b**, 1725) as indicator. Although the *p*H values at which the colour-changes of these indicators take place are different, the end-points observed, in the titrations of *N*/10 hydrochloric acid or sulphuric acid with sodium hydroxide (not carbonate-free) agree with the end-point in visual light with phenolphthalein as indicator. We find the end-point with R-salt (Desha, Sherill and Harrison, *J. Amer. Chem. Soc.*, 1926, **48**, 1493) to be the same as in the above titrations. We find also that magnesium 8-hydroxyquinoline complex can be used as an indicator in a similar way. The indicator is prepared by heating on a steam-bath 0·1 g. of magnesium-oxine complex with 10 ml. of *N*/10 hydrochloric acid and 100 ml. of water for half-an-hour; the solution is then made up to 100 ml. with water and filtered; 3 to 5 drops of this solution are used for a titration. In titrating solutions of acids, a change from colourless to golden-yellow takes place at the end-point, which is reached at the same value as for the above indicators. Neither hydroxyquinoline nor its hydrochloride fluoresces in this way, and the change in fluorescence is doubtless due to the formation of the magnesium-oxine complex at about *p*H 7.

Certain silver nitrate titrations, using adsorption indicators, can be carried out similarly in ultra-violet light. In the titration of chlorides (approx. N/40) with dichlorofluorescein (2 to 4 drops of 0·1 per cent. solution) as indicator, a colour-change takes place at the end-point from a fluorescent yellow-green to a chocolate-coloured suspension in which the fluorescence is extinguished. If the silver nitrate solution is added in a rapid stream, the end-point agrees exactly with that obtained in visual light with this indicator. In the titration of bromides or iodides (*N*/40 approx.) with eosin (2 ml. of 0·1 per cent. solution) as indicator, the change from a fluorescent golden solution to a non-fluorescent chocolate-coloured suspension agrees with the end-point in daylight. Phenosafranine, which shows a change from pink to blue on the precipitate in daylight, does not exhibit any change in ultra-violet light.

In the above titrations the values at which the end-points are reached depend upon the rate of addition of the silver nitrate and the amount of indicator used. The following figures illustrate this:

Sodium chloride ($N/50$, 100 ml.) was titrated with silver nitrate ($1{\cdot}005N/10$), the silver nitrate being added from the burette in a fine steady stream. Dichlorofluorescein (0·1 per cent. solution) was used as indicator.

Vol. of indicator in ml.	0·1,	0·2,	0·3,	0·5,	0·75,	1·0,	2·0
Titre in ml.	12·5,	16·3,	18·0,	18·6,	19·7,	19·9,	20·2

Slow addition of the silver nitrate, as in this set of experiments, caused only a gradual disappearance of the fluorescence; when 2 ml. of indicator were used, fluorescence persisted in the liquid after the precipitate had settled.

If the silver nitrate solution is added rapidly from the burette, as recorded above, satisfactory and sharp end-points are obtained. The colour-changes are not so striking as in the acidimetric processes, and it is obvious, from the above results, that this type of titration could be of only limited application.

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NOTES ON THE DETERMINATION OF BISMUTH IN COPPER

The results of experimental work carried out during the last two years on the effects of bismuth on metallic copper and its elimination by heating the solid metal in currents of various gases throw some light on the mechanism of the method of Colbeck, Craven and Murray for the determination of bismuth in copper (Analyst, 1934, **59**, 395).

It has been found that when copper containing small quantities of bismuth is heated in a current, not only of hydrogen, but also of nitrogen, carbon monoxide or coal gas, at suitable temperatures and for sufficient time, the bismuth is entirely eliminated and carried forward. This negatives the formation of a hydride, and indicates that the mechanism of removal consists in outward passage of the bismuth from the copper and its distillation or sublimation from the surface in a current of inert or reducing gas.

The temperature at which this distillation begins is quite low, the first actual loss in hydrogen or nitrogen taking place at 500° to 550° C. At such a low temperature too long a time would be required for the total elimination of bismuth, but, on the other hand, too high a temperature must be avoided, as immediately even incipient fusion takes place the elimination of bismuth from the fused portions ceases.

The method for coarse particles of copper given by Colbeck and his collaborators (*supra*) (*i.e.* fusion at 1100–1120° C.) has never, in our hands, effected complete elimination of the bismuth; for example, copper containing 0·0056 per cent. of bismuth was heated in hydrogen to 1100° C. and melted, and, after being thus heated for two hours and allowed to cool in the furnace, the residual copper was found to retain 0·0035 per cent. of bismuth. This was confirmed by experiments carried out by Dr. Brislee, who found it impossible to eliminate any bismuth from molten copper by passing a stream of hydrogen or ammonia through the metal. (Private communication from Dr. F. J. Brislee of Messrs. British Insulated Cables, Ltd.)

It has been found that, with copper in a state of suitably fine division, a temperature of 950° to 1000° C. is the most efficient, and that when pure dry nitrogen or hydrogen is used, two hours' treatment, with a flow of about four l. per hour, is necessary for the process.

The size of the copper sample is of considerable importance, total elimination of the bismuth taking place with ordinary fine turnings, ground to pass a 20-mesh sieve and to be retained by a 30-mesh sieve; with copper wires of various diameters, total elimination was effected in two hours in hydrogen at 950° C. with wire of diameter up to, but not above 0·025 in.

We consider that the temperature given in the above-mentioned paper for copper millings, *viz.* 1050° to 1060° C., is too high for most brands of copper, as incipient fusion is liable to take place, causing retention of bismuth in the sample, and so leading to low results when used as a method of analysis; also that 1 hour is not sufficient for total elimination of the bismuth.

Some results on wire-bar copper are given in the following table:

WIRE-BAR COPPER (Original bismuth-content = 0·0056 per cent.)

Two hours' treatment at the following temperatures (heating up and cooling down in the furnace) °C.	Bismuth-content after treatment in hydrogen Per Cent.	Bismuth-content after treatment in nitrogen Per Cent.	Percentage of original bismuth eliminated in hydrogen	Percentage of original bismuth eliminated in nitrogen
450	0·0056	0·0056	Nil	Nil
550	0·0038	0·0042	32·1	25·0
650	0·0035	0·0023	37·5	58·9
750	0·0025	0·0011	55·3	80·3
850	0·0010	0·0006	82·1	89·3
950	Nil	Trace	100·0	100·0
1000	Nil	Nil	100·0	100·0
1050	0·00143	0·00185	74·4	66·9
1100	0·0034	0·0037	39·3	33·9

The optimum temperature to be used depends to some extent on the quality of the copper; *e.g.* with wire-bar copper of good quality there was total elimination in hydrogen and nitrogen after two hours at 950° C., whilst at temperatures above 1000° C. total elimination was not obtained. With blister copper containing cuprous oxide total elimination of bismuth was also effected in hydrogen at 950° C., but when nitrogen was used there was total elimination at as low a temperature as 870° C.

For the colorimetric determination of bismuth in copper the iodide method has been used, modified by the addition of 0·25 g. of ferrous ammonium sulphate per 10 g. of sample, the iron acting as a collector for the bismuth when it is precipitated with sodium carbonate. After this precipitation it is necessary to boil the liquid for ten minutes and to allow it to stand for at least six hours, or preferably overnight, before proceeding with the filtration, etc. Under these conditions perfect agreement is obtained between the direct colorimetric method and the mirror method.

For electrolytic copper and for various brands of commercial copper the chemical separation of the bismuth is preferred to the mirror method. (See also *Bull. Inst. Mining and Metall.*, No. 363, Dec., 1934.)

C. O. BANNISTER
W. M. DOYLE

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METALLURGY DEPARTMENT

THE DETERMINATION OF FREE SILICA IN COAL-MEASURE ROCKS

BEING engaged upon the examination of a ground shale used for stone-dusting in a New Zealand coal-mine when Shaw's paper (ANALYST, 1934, **59**, 446) appeared, I tried the method recommended, and the results may be of interest.

The only variation introduced was the use of a 1500-ml. Pyrex beaker in place of a porcelain dish; all digestions were carried out on a hot plate. After each acid treatment the contents of the beaker were allowed to settle overnight, but in subsequent treatments with Lunge's solution two hours' settling was sufficient. The use of a syphon was found satisfactory.

In a preliminary determination the percentage of free silica obtained was 14·6. Duplicate determinations were then made, and the results were 13·8 and 14·1 per cent., respectively.

This confirmed the author's statements as to the reliability of the method.

L. R. L. DUNN

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Official Appointments

THE Minister of Agriculture and Fisheries has approved the following appointments:

RHYS PENDRILL CHARLES as Agricultural Analyst for the County Borough of Bournemouth, in place of R. A. Cripps (retired).

THOMAS REGINALD HODGSON as Agricultural Analyst for the County Borough of Stockport, in place of W. Marshall (deceased).

HENRY TURNER LEA as Agricultural Analyst for the County Borough of Huddersfield, in place of L. G. Paul (resigned).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1934

OF the 1186 samples submitted under the Sale of Food and Drugs Acts, 1143 were bought informally. The 43 formal samples were samples of milk.

FAT IN SHREDDED SUET. SOYA-BEAN FLOUR IN SUET.—The label of a sample contained the words "1½ lbs. equals 2 lbs. of raw suet." The amount of fat present was 94 per cent., which approximates to the amount found in ordinary butcher's suet. Some years ago samples of suet obtained from butchers were analysed, the suet being stripped from the membrane as it would be in an ordinary household. It was found that the amount of fat in the portion separated varied from 93·4 to 97·2 per cent., with an average of 95 per cent. of the whole bulk of the material. The separated membrane contained only small amounts of fat, varying from 1·0 to 4·7 per cent. of the total bulk of the sample.

For 1½ lbs. of the shredded suet in question to be equal to 2 lbs. of raw suet, the latter would have to contain only about 70 per cent. of available fat, and this would be the case only if there had been extraordinary carelessness in separating the membrane from the suet. Representations were made to the firm packing the suet, and they have agreed to cease using the label in its present form.

A further claim was made for this article. It was stated to be free from starch and to contain "a pure food product introducing valuable proteins, carbohydrates and vitamins." This material, which was used in place of the usual rice flour for separating the shreds of suet, was found to consist of soya-bean flour which, of course, does not contain starch and has a definite food value as a source of protein and vitamin *A*.

GREY POWDER TABLETS.—A sample of half-grain grey powder tablets was deficient in mercury and in chalk to the extent of 15 per cent. Although there is a tendency for mercury to volatilise from tablets such as these, yet, as the deficiency for both mercury and chalk was the same, it seemed more probable that the initial amounts of both ingredients were too small. The suppliers were cautioned.

H. H. BAGNALL

CITY OF LONDON

ANNUAL REPORT OF THE PUBLIC ANALYST FOR 1933

THE Report of the Public Analyst (Mr. A. J. C. Lickorish, F.I.C.) is included as a section of the Report of the Medical Officer of Health of the City of London.

Of the 1012 samples of food and drugs examined, 807 were informal samples, and 17 of these were condemned.

ICE CREAM.—The consumption of ice cream has greatly increased during the past few years, and it is to be regretted that there is no legal definition or standard of quality for it. Analyses of the 28 samples taken in the City showed a very wide range in the percentage fat-content, which bore little relationship to the prices charged. Thirteen of the samples, purchased at restaurants, had a fat-content of 8 per cent. or more, ranging from 8·5 per cent. to 24·4 per cent., with an average of 13·5 per cent. Fifteen samples, taken principally from itinerant vendors, had a fat-content ranging from 0·6 to 4·6 per cent., with an average of 2·6 per cent.

It may reasonably be submitted that ice cream should have a milk-fat content of at least 8 per cent., and should consist only of butter fat, milk solids-not-fat, sugar, gelatin and water. Mixtures consisting mainly of milk, sugar, cornflour, eggs, etc., should be permitted to be sold, not as ice cream, but under an appropriate designation, such as Ice or Ice Custard.

GLYCERIN OF ALUM.—An informal sample was found to be deficient, to the extent of 13·3 per cent. in alum, and the deficiency in the subsequent formal sample was 15 per cent. The vendor was cautioned.

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

DESCRIPTION OF BRANDED ARTICLES

Ammoniated Quinine Tablets

On November 30th a pharmacist was summoned at the West London Police Court for supplying ammoniated quinine tablets containing no ammonia. Mr. H. Glyn-Jones, for the defence, pleaded that his client had committed an unintentional offence, in that he had bought the goods on a warranty, nine months before the retail purchase took place. He gave an undertaking that the defendant would not sell any tablets of this nature in future without taking care, as far as possible, that the goods corresponded with their description, and the magistrate (Mr. Marshall) thereupon dismissed the case on payment of £3 3s. 0d. costs.

Department of Scientific and Industrial Research

REPORT OF THE WATER POLLUTION BOARD

For the Year ended 30th June, 1934*

In the Seventh Annual Report of the Water Pollution Research Board reference is made to the exceptional conditions of weather during 1933 and 1934. The long spell of dry weather not only caused difficulties in the provision of ample quantities of water for various purposes, but also had a serious detrimental effect on the quality of the water in rivers and streams into which sewage and trade effluents are discharged, as less water than usual was available for dilution of the discharges. At the present time there are many undertakings utilising polluted river water, after treatment, for domestic and industrial supplies, and there is no doubt that other polluted rivers will have to be similarly utilised in the future to meet the increasing demands of the community. It is important, therefore, that further efforts should be made to prevent, as far as possible without unnecessary expense, the pollution of rivers and streams and other sources of water supply if expensive methods of water treatment and danger to public health are to be avoided. This necessitates intensive, systematic research, as in many cases entirely satisfactory methods of treatment and disposal of trade effluents at a reasonable cost are not known. Further, as industry develops, new processes of manufacture are devised and new methods of dealing with the waste waters will be required.

The investigations initiated by the Board may be divided into four main groups dealing, respectively, with purification of water for public supply, methods of treatment and disposal of sewage, methods of treatment and disposal of trade effluents, and various problems of river pollution.

Base-Exchange Process of Water Softening.—In experiments on the use of commercial base-exchange materials for softening waters containing calcium bicarbonate, calcium sulphate and magnesium sulphate, it was found that the base-exchange values of the treated minerals, kenzelite and natrolith, were respectively equivalent to about 0·4 and 0·6 lb. of calcium oxide per cu.ft. of material; they were approximately the same for hard waters containing magnesium salts as for those containing calcium salts. The base-exchange value of doucil (a synthetic material) was equivalent to about 1·0 lb. of calcium oxide per cu.ft. with hard water containing calcium salts, but only to about 0·7 lb. with solutions of magnesium sulphate.

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* H.M. Stationery Office, Kingsway, London, W.C.2. 1934. Pp. 44. Price 9d. net.

In attempts to determine the conditions of equilibrium between zeolites of alkali and alkaline earth metals, true conditions of equilibrium were not attained even after circulation of the solutions over the prepared zeolites for several weeks.

Many samples of British clays have been treated by various methods, and in a few instances substances with base-exchange values greater than those of some imported commercial materials have been obtained.

CONTAMINATION OF WATER BY LEAD.—A summary of existing knowledge on the action of water on lead has been published as Water Pollution Research Technical Paper No. 4 (*cf.* ANALYST, 1934, **59**, 346). Experiments have been made to determine how far tests under apparently similar conditions may be expected to give results in close agreement. In some cases the quantity of lead removed from standard lengths of commercial lead piping by distilled water in 24 hours agreed well; in others there were wide differences in the results. In experiments in which flat rectangular plates of lead were immersed in flasks of distilled water for definite periods of time there was fair agreement in the quantities of lead removed by the water.

MILK FACTORY EFFLUENTS.—Further progress has been made in experiments at Rothamsted (*cf.* ANALYST, 1934, **59**, 282) on the conditions affecting the purification of effluents containing milk by a process involving anaerobic fermentation followed by biological filtration. Anaerobic fermentation of mixtures containing 1 per cent. of milk in water causes separation of the fat and of some of the protein. The separated liquid can then be readily oxidised in percolating filters, with an efficiency of oxidation of about 99 per cent. Experiments have also been carried out on the treatment of milk by the activated sludge process. Several creameries and factories have been visited, and an outline is given of the methods in use for the treatment and disposal of the liquid effluents.

BIOLOGICAL OXIDATION OF FATS AND SOAPS.—Experiments at the Rothamsted Experimental Station on the biological filtration of solutions of sodium stearate, alone and in admixture with domestic sewage, have shown that soap in concentrations as high as 25 parts per 100,000 in sewage is readily oxidised in percolating filters.

SEWAGE DISPOSAL.—In the investigation being carried out for the Department at the London School of Hygiene, Barcroft respirometers have been employed in experiments on the effects of various factors on the rates of oxidation of sewage, sewage effluents, and activated sludge in contact with air at 24° C. Under the conditions employed the rates of oxidation of sewage and sewage effluents were greater than under the conditions ordinarily adopted in the test for biochemical oxygen demand. It was also found that the rate of oxidation of mixtures of sewage and activated sludge is greater than the sum of the rates for the separate constituents, especially during the early stages of oxidation. Maximum rates of oxidation for sewage and effluents were obtained at *p*H values between 6·6 and 9·0 and for activated sludge at *p*H values between 6 and 10. It has been shown that sewage and sludge previously sterilised by heating, by filtration through a Seitz filter, or by treatment with certain disinfectants do not absorb oxygen from air. Inoculation of the sterilised sewage or sludge by the addition of small quantities of untreated sewage or sludge or of washed suspensions of certain bacteria at once initiates absorption of oxygen.

The addition to sewage of potassium cyanide in concentrations ranging from *M*/200 to *M*/10,000 considerably reduced the rates of oxidation of the sewage by air at 24° C. during the first five hours. After this period the effect of the cyanide gradually decreased until the rate of oxidation became the same as for the sewage alone.

In view of the presence of protozoa in percolating filters at sewage works and in sewage undergoing treatment by activated sludge, experiments have been made to ascertain the effect of *Polytoma uvella* on the oxidation of sewage and sewage sludge by air. It has been found that this protozoan flagellate initiates the oxidation of previously sterilised sewage, but not so actively as certain bacteria.

The oxidation of solutions of an ammonium salt, sugars, amino acids, formate, lactate, glycerol, olive oil and phenol in the presence of activated sewage sludge has also been studied. The rate of oxidation of ammonia in the presence of activated sludge reached a maximum when the *p*H value was between 8·0 and 9·2. In the concentrations employed and in the presence of activated sludge, all the organic substances used, with the exception of phenol, were oxidised.

The investigation of the nature and amount of the colloidal and other dispersed matter in sewage has been continued for the Department at University College, London, under the immediate direction of Professor F. G. Donnan. During the past year the work has included experiments on the flocculation or coagulation of dispersed matter by passing finely-divided streams of air, oxygen, hydrogen, and nitrogen through samples of domestic sewage at 25° C. It has been shown that all four gases have a similar effect in causing, in a few hours, coagulation of a considerable amount of the dispersed material. Even particles originally so small as to pass an ultra-filter were coagulated by the action of the bubbles of gas.

RIVER MERSEY INVESTIGATION.—Considerable progress has been made in the work of the River Mersey investigation which was begun in April, 1933, with the object of determining the effect of discharges of crude sewage into the estuary on the amount and nature of silt and other solid matter deposited. The banks exposed at low tide have been surveyed and classified into two groups according to whether they are covered by sand or by mud. An attempt has also been made to determine the relative stabilities of the different banks from the changes in size and position as shown by the surveys since 1861, and from a biological survey of the banks; areas subject to frequent change as a result of tidal action are not likely to support certain types of organisms. The chemical section of the work has included the examination of samples of water from all parts of the estuary at different depths and at various states of the tide and the examination of numerous samples of solid matter from exposed banks. The material of the mud bank near Mount Manisty appears to be a mixture of sand and clay; the proportion of clay in this bank is greater near the shore, where the tidal currents are probably weakest. In general, the concentration of organic matter increases with the proportion of clay and with a decrease in the average size of the particles. The carbon-content rarely exceeds 3·5 per cent. of the dry weight of the mud.

Information has also been collected with regard to the quantity and nature of the discharges of sewage and trade effluents into the estuary.

GAS WORKS EFFLUENTS.—The Liquor Effluents and Ammonia Sub-Committee of the Institution of Gas Engineers has continued its investigations on the disposal of effluents from gas works, and has issued a third report on the results obtained. It cannot be assumed that the acid permanganate test measures the relative effects of constituents of gas liquor effluents on biological methods of sewage purification. For this reason the Committee has begun a comprehensive investigation on the biological oxidation, by percolating filters and the activated sludge process, of sewage to which known quantities of gas liquor effluents and their various constituents have been added. These experiments have indicated that sewage to which phenol, thiocyanate or catechol (representing higher tar acids) has been added, even in amounts sufficient to increase the oxygen absorption value of the sewage by 32 parts per 100,000, is readily oxidised by biological filtration. Under the conditions of the experiments, the quality of the effluents from the filters was not appreciably affected by the addition of any one of these three constituents. Thiosulphate and sulphide added in amounts sufficient to increase the oxygen absorption values of the sewage by 16 to 32 and 8 to 16 parts per 100,000, respectively, caused deterioration in the quality of the effluents, but had little effect in smaller concentrations. It was found necessary to increase the concentration of added thiocyanate and thiosulphate gradually, otherwise the quality of the treated effluent deteriorated for a time, presumably until suitable organisms had developed in sufficient numbers on the filtering medium.

Queensland

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDED JUNE 30TH, 1934

In his Annual Report the Government Analyst (Mr. J. B. Henderson) states that 12,217 samples were examined, this being a record number. Of these, 6314 were for the Health Department, 2079 for the Customs, and 1511 for the Geological Survey. The 2447 samples of foods submitted by inspectors under the provisions of the Health Acts included 2259 of milk, 127 of fresh fruit, 30 of spirituous liquor, and 20 of meat (sausage and minced). Of these, 491 (351 milks) were condemned. Twelve of the 50 disinfectants, 19 of the 59 drugs and medicines, and 16 of 23 toilet preparations were condemned, mostly for mislabelling, the contents of the packages not justifying the claims on the label.

STANDARDS FOR BREAD.—Sixty-one samples from that number of bakeries in the Brisbane area were examined. Only 2 samples (with 45·7 and 45·4 per cent.) contained water in excess of the maximum allowance of 45 per cent. of water laid down in the standard. In the other samples the amounts of water ranged from 41·8 to 45 per cent., the average being 43·8 per cent. All the samples were normal with regard to crust, colour, pile, texture and flavour.

AMMONIACAL CANNED FISH.—Twenty-six of 38 samples of imported canned fish, mostly sardines and sild, were condemned because of decomposition or excessive tin-content. All the samples high in tin were markedly alkaline in reaction, some containing free ammonia. Even fresh stock was found to be ammoniacal shortly after arrival, this suggesting that the fish was in a state of incipient decomposition when packed.

LEAD ARSENATE IN VEGETABLES AND FRUIT.—Eleven consignments of cabbage contained lead arsenate in material quantity, the highest proportion found being 4·8 grains per pound. There has fortunately been a marked reduction recently in the use of lead arsenate on vegetables, as compared with previous years.

Of 246 samples of apples and pears taken from consignments from Southern States, 57 contained less than 1-100th part of a grain of arsenic to the pound, and 189 contained over this proportion, the highest figure being a quarter of a grain per pound. These samples were taken because they showed the presence of spray residues on the skins, and so do not afford much evidence of the actual proportion of fruit coming forward that is contaminated with arsenic. The British authorities placed a limit of 1-100th part of a grain of arsenic to the pound on imported fruit, and this limit has tentatively been adopted in Queensland. It is unfortunate for both public and growers that this dangerous practice of using poisonous insecticides cannot be stopped. It affects the public because it renders the foods poisonous, and affects the growers because the public buy less, being afraid of the poison.

ARSENIC IN TOBACCO.—The use of lead arsenate on tobacco plants, both in Australia and overseas, has led to the examination of all tobacco sold either in leaf or in the manufactured form. Of the 2664 samples examined, the great majority were free from, or showed only traces of, lead arsenate. Experiments have shown that, although most of the arsenic in contaminated tobacco is left in the ash, if there is more than a trace of lead arsenate in the tobacco, some passes over in the smoke. All consignments showing more than a trace are therefore condemned. As buyers do not buy leaf until it has been certified as conforming to the Health Department's requirements, all batches have to be tested; hence the recent large increase in the number of tobacco samples.

ARTIFICIAL COLORATION OF FRUIT BY MEANS OF GASES.—The practice of leaving green, unripe fruit for a short time, generally overnight, in an atmosphere containing certain gases has recently been widely adopted. Several gases have been used for the purpose, even the exhaust gases from motor engines, and several kinds of fruit are treated. The great bulk of citrus fruits are now being changed from a green to a yellow colour in this way, while a proportion of the bananas and pineapples are also being treated. The appearance of ripeness, however, is entirely fictitious, except when the gas is used as part of a complete ripening process. When used by itself, the treatment leaves green, sour, unripe oranges, still sour and unripe, and hard unripe bananas still hard and unripe, despite their deceitful, attractive yellow skin. There is no question that in such cases the practice is fraudulent, as the sole object is to give unripe fruit the appearance of being ripe, and so to deceive the buyers. Unfortunately, the problem of determining when a fruit is really ripe, by definite chemical tests, has not yet been solved. There is, however, already evidence that some consumers are noticing the unripe quality of certain fruits of ripe appearance, and are buying less fruit, owing to the difficulty of obtaining it in an edible condition. This loss of market may help to stop the practice, but in the best interests of the consumers, and therefore also of the growers, the problem created by the new fraud might be met by a new regulation definitely prohibiting such misleading artificial colouring.

LEAD IN PAINTS FOR GATES AND RAILINGS.—Under the Health Acts the use, for verandah rails, gates or fences, of paints containing more than 5 per cent. of soluble lead is not permitted. The proportion of soluble lead is determined by treating the paint pigment with a 0·25 per cent. solution of hydrogen chloride, this strength being equivalent to the hydrochloric acid content of normal gastric juice. Of 91 samples of paint examined from verandah rails or fences, 67 exceeded the limit of 5 per cent. of soluble lead.

CORROSION OF RABBIT-PROOF FENCES.—Analyses of 26 samples of both old and new nettings, some only slightly corroded and others badly corroded, and of 26 samples of the soils in which they had been buried, gave no conclusive evidence as to the reasons for the short life of some of the nettings. The evidence obtained was not sufficient to support final recommendations for preventing the trouble. One striking result was obtained with regard to the effect of laying new wire netting in contact with the old rusted netting left in the ground. In the presence of ordinary soil water the new and rusted metals in contact give rise to quite marked electrical currents, and the corrosion of the new metal in such cases is very rapid—much more rapid than was expected. At a conference of representatives of the Lands Department, the Leichhardt Rabbit Board, and the Government Analyst it was decided to erect test panels in various localities in order to determine the relative importance in improving the life of the netting of—(i) Elimination of the possibility of electrolytic action between new and old netting; (ii) the use of a bituminous coating on the netting; and (iii) the use of heavier gauges of netting; and also (iv) to compare Australian and imported nettings. Eight sites with varying conditions of soil types and soil moisture and salinity have been selected, and a comprehensive series of test panels will shortly be erected.

Scientific Glassware Standards

B.S.I. SPECIFICATIONS FOR DISTILLATION FLASKS AND FOR GROUND-GLASS JOINTS

The British Standards Institution has issued specifications for distillation flasks and for interchangeable conical ground-glass joints. These are the first glassware specifications to be issued by the Scientific Glassware Committee, which was taken over from the Institute of Chemistry when the Chemical Division of the Institution was formed.

Distillation Flasks Specification (No. 571)

This specification provides for a complete series of fourteen flasks ranging from a distillation capacity of 30 ml. to 3000 ml. Prior to the publication of the specification, four manufacturers were making, between them, over this range of capacity, flasks having twenty different nominal capacities, and having forty different bulb capacities. The general adoption of the standard series will, therefore, not only diminish the different sizes of flasks now being made, but will also ensure identity of actual capacity between flasks having the same nominal capacity.

Nominal Capacity and Distillation Capacity.—The following three conditions are fulfilled by each flask in the series: (1) the centre of the side-tube is 75 mm. from the top of the neck; (ii) the centre of the side tube is 90 mm. from the liquid surface when the flask is vertical and contains a quantity of liquid equal in volume to the distillation-capacity of the flask; (iii) the bulb-capacity is 30 per cent. greater than the distillation capacity.

The first condition ensures the same immersion of the stem of the thermometer in each size of flask, the thermometer being placed so that the top of the bulb is level with the bottom of the side-tube at its junction with the neck. Thermometers calibrated for 100 mm. immersion are convenient for use with the flasks. When the thermometer is fixed as directed above, the immersion line of the thermometer will be in the neighbourhood of the top of the cork holding the thermometer in position in the neck.

The second condition helps to secure reproducibility of results in distillation by ensuring that the thermometer-bulb is at a constant distance from the level of the liquid surface at the beginning of a distillation. The third condition ensures a definite bulb-capacity for each nominal capacity, the bulb-capacity being taken as 30 per cent. greater than the distillation-capacity. Considerable variation was found in the bulb-capacity of flasks from different sources having the same nominal capacity.

Specification for Ground-Glass Joints (No. 572)

This specification has been prepared to secure the interchangeability of conical ground-glass joints in laboratory and industrial glassware. In order to ensure interchangeability, the following elements have been specified for each joint: (i) Taper; (ii) diameter of larger end of socket; (iii) diameter of smaller end of cone; (iv) length of ground portions of cone and socket. A taper of 1 in 10 on diameter, equivalent to a cone semi-angle 2° 51′ 45″ has been adopted for all joints.

To meet the requirements of different types of apparatus, four series of standard joints, designated Series A, Series B, Series C and Series D, have been provided. The dimensions for the standard Series A have been chosen to fit in with foreign standards already in existence. Joints in the additional series have the same diameter at the larger end as the corresponding joints in Series A, but have different lengths of engagement; thus, Series B, three-quarters; Series C, a half; and Series D, a quarter the length of Series A.

The four series of joints together afford a very wide choice, so that provision is made for the replacement of existing joints and for special requirements. It is considered, however, that the following sizes would meet almost all normal requirements: A 14, A 16, A 19, A 24, A 29; B 24, B 29, B 34, B 40, B 45, B 50. It is, therefore, recommended that these sizes be adopted for general use, and that the remaining sizes be employed only when it is impossible to use one of the recommended sizes.

The dimensions and tolerances specified were adopted only after very careful measurement and examination, at the National Physical Laboratory, of conical ground-glass joints in present-day use.

Copies of these specifications (Nos. 571 and 572—1934) can be obtained from the Publications Department, British Standards Institution, 28, Victoria Street, London, S.W.1, price 2s. 2d. each, post free.

Standardisation of the Methods of Testing the Fastness of Dyed Materials*

THE Report of the Fastness Committee of the Society of Dyers and Colourists deals with three fastness requirements, *viz.* (i) fastness to light; (ii) fastness to perspiration; (iii) fastness to washing.

FASTNESS TO LIGHT.—The Committee adheres to the international practice of employing 8 grades of fastness to light (*cf.* ANALYST, 1934, 59, 784). The standard dyes selected are as follows:

Red Standards.—(2) 0·5 per cent. Acid Magenta IIS (I.C.I.) (C.I.692); (3) 0·5 per cent. Polar Red 3B Conc. (Gy.); (4) 1 per cent. Cloth Fast Red R (S.C.I.); (5) 1 per cent. Alizarine Rubinole GW (I.G.) (C.I.1091); (6) 1 per cent. Kiton Fast Red 4BL (S.C.I.); (7) 1·2 per cent. Alizarine Orange A425 Powder (I.C.I.) on zinc (C.I.1033); (8) Durindone Red B400 Powder (I.C.I.) (C.I.1207).

Blue Standards.—(2) 0·5 per cent. Lissamine Violet 6BNS (I.C.I.) (C.I.717); (3) 0·6 per cent. Brilliant Indocyanine 6B (I.G.); (4) 1·1 per cent. Polar Blue G. Conc. (Gy.); (5) 0·5 per cent. Solway Blue R.S. (I.C.I.) (C.I.1076); (6) 2 per cent. Alizarine Light Blue 4GL (S.); (7) 4 per cent. Caledon Blue GCP300 Powder (I.C.I.) (C.I.1113); (8) 3 per cent. Indigosol Blue AGG (D. & H.).

FASTNESS TO PERSPIRATION.—It has been found possible to make up artificial test solutions representing acid and alkaline perspiration, based on the results obtained by Voss and McSwiney in their investigations on the composition of human sweat (*cf.* ANALYST, 1934, 59, 496). These solutions are:

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* Obtainable from the Secretary, The Society of Dyers and Colourists, 32, Piccadilly, Bradford, Yorkshire. Price 7/6 net.

Acid Perspiration Liquor.—2·65 g. of sodium chloride and 0·75 g. of urea per l., brought to *p*H 5·6 with *N*/10 acetic acid.

Alkaline Perspiration Liquor.—0·839 g. of ammonium chloride, 1·732 g. of sodium chloride and 0·424 ml. of ammonia solution (sp.gr. 0·88) per l., brought to *p*H 7·8 with *N*/10 acetic acid.

A schedule of tests is given indicating the manner in which these solutions should be used.

FASTNESS TO WASHING.—"Four tests of increasing severity are prescribed and cover all degrees of severity from a mild home wash to a test representing the cumulative action of several severe power washes." Two sets of standards are then given, one in the red series and the other in the blue.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Cold Storage of Poultry. Chemical Changes in the Fat of Gas-stored Chickens. C. H. Lea. (*J. Soc. Chem. Ind.*, 1934, **53**, 347–349.)—Young birds (12 weeks old) were stored in carbon dioxide and in air at 0° to −1° C. The fat was extracted from the minced skin with petroleum spirit, and from the minced breast muscle with peroxide-free ether; the solvent was distilled and the last traces removed *in vacuo* below 50° C. The figures for free acidity of the fat show a rapid rise coincident with appearance of mould on the air-stored samples, but a much slower development of acidity in the fat of gas-stored birds. For the determination of peroxide oxygen 1 g. of the skin fat, or the whole of the muscle fat (about 0·5 g.), was heated with powdered potassium iodide in a mixture of glacial acetic acid and chloroform (20 ml.), and the liberated iodine was titrated with 0·002 *N* thiosulphate solution, all operations being carried out in the dark or in weak artificial light to prevent oxidation of the fat. The amount of fat recovered from the skin samples was 9 to 21 per cent., and from breast muscle 0·16 to 0·35 per cent. Determinations of peroxide oxygen in the breast fat gave zero values throughout the carbon dioxide experiment; in the air experiment at 17, 24, and 46 days values of 3, 3 and 5 ml. per g. of fat, respectively, were obtained. It must be remembered that a considerable proportion of linolic acid is present in chicken fat, and also that in young chickens the proportions of fat are small. It is concluded that, whilst carbon dioxide practically eliminates mould and bacterial spoilage in chickens at 0° C., autolysis of the tissues by enzymes prevents prolongation of storage-life for undrawn birds. After long gas-storage periods oxidation of the fat may cause spoilage unless the carbon dioxide concentration closely approaches 100 per cent. D. G. H.

Scheme for the Approximate Determination of the Proteins of Muscle. E. C. Smith. (*J. Soc. Chem. Ind.*, 1934, **53**, 351–354T.)—A method has been worked out for the determination of the more important fractions of muscle protein, viz.: (i) Intracellular proteins, these being myogen, which is soluble in both water and salt solutions, and myosin, which is soluble only in salt solutions. (ii) Extracellular proteins (insoluble in water or salt solutions): collagen, which is converted into water-soluble gelatine when heated, and elastin, which is resistant to the action of trypsin. The efficiency of a solution for extracting the soluble proteins depends not only on the ease with which a protein dissolves in the solvent, but also on the effect of the solvent on the cell-walls and connective tissue, which hinder penetration of solvent and escape of solution. Tests made with a number of salt solutions show that 10 per cent. ammonium chloride solution is the most effective solvent. Six extractions, with continuous gentle agitation, assisted by occasional grinding with sand, remove about 95 per cent. of the total extractable protein, and much time is saved and little error involved by limiting the number of extractions to six.

The extraction is carried out by placing four 5-g. lots of the minced and mixed muscle in four 50-ml. centrifuge cups, together with 35 ml. of cold 5 per cent. magnesium sulphate (or 10 per cent. ammonium chloride) solution and 10 g. of washed sand. The muscle is ground for 3 minutes with a flattened glass rod, and the tubes are then closed with rubber stoppers and shaken in a horizontal position for 30 minutes at 0° C. at such a rate that little froth is formed. The suspension is centrifuged and, after the clear supernatant layer has been transferred to a flask, the extraction and grinding are repeated, six such operations being performed.

To determine myosin, 10 g. of the protein sol are poured into 100 ml. of ice-cold water in a centrifuge cup and well stirred, the protein separating as an opalescent gelatinous precipitate. After being kept at 0° C. for not less than 4 or more than 18 hours, the liquid is centrifuged. Any floating particles are removed to a filter, and the residue is washed three times on the centrifuge with water and then with 10 per cent. trichloroacetic acid solution to ensure complete removal of ammonium salts. The precipitate in the centrifuge cup and the filter-paper (washed similarly) are transferred to a Kjeldahl flask and the nitrogen is determined as usual; triplicate determinations should be made. The myosin determined in this way in solutions containing between 0·15 and 0·13 per cent. of myosin-nitrogen is 88 ± 2 per cent. of that present; myogen interferes appreciably only when present at a concentration six times that of the extracts made as described. The non-myosin extractable protein is regarded as consisting almost entirely of myogen. There is said to be a third protein, globulin X, present, but this is probably only a small fraction of the total. The pigments, haemoglobin and myoglobin, may be determined by the usual physiological methods.

The insoluble residues remaining after extraction with ammonium chloride or magnesium sulphate are washed with 80 ml. of water into a 200-ml. beaker and autoclaved for 2 hours at 2 atmospheres' pressure (121° C.). The hot liquid is filtered and the residue on the filter is washed with boiling water until the wash water shows practically no biuret reaction. The nitrogen in the filtrate is collagen-nitrogen. The undissolved residue is washed back into the beaker with 25 ml. of water, and 25 ml. of a solution of trypsin (0·2 g. of B.D.H. trypsin and 0·6 g. of sodium carbonate in 100 ml. of water) are added. The suspension is digested for 16 hours at 37–40° C. and then boiled, and the precipitate is filtered off and washed. The nitrogen in the filtrate is residual intracellular protein-nitrogen (plus that introduced with the trypsin solution), whilst that in the precipitate is elastin-nitrogen.

This method has given concordant results on triplicate samples. When the residual intracellular fraction is large, there is evidence of a small loss of nitrogen from this fraction, possibly by evolution of ammonia during the digestion. Results of partial and complete analyses of rabbit and ox muscle are given. During storage of the muscle, the residual intracellular fraction increases, owing to part of the protein becoming insoluble, but the rate and extent of this change are much less than have been recorded by others. T. H. P.

Cassava Products from British Honduras. (*Bull. Imp. Inst.*, 1934, **32**, 370–374.)—Samples of cassava starch and of dried cassava root (chips) from British Honduras were analysed. Sample (*a*) consisted of slices of scraped roots assumed to be sweet cassava chips, creamy-white in colour with an occasional brown tinge; (*b*) assumed to be dried bitter cassava chips consisting of slices of scraped roots rather browner than (*a*); (*c*) Stann Creek sweet cassava starch—a white powder and small creamy-tinted lumps; and (*d*) similar to (*c*), but of a better colour. The composition of the samples was as follows:

	(*a*) Per Cent.	(*b*) Per Cent.	(*c*) Per Cent.	(*d*) Per Cent.
Moisture	12·3	12·1	14·2	13·9
Crude proteins	1·0	1·0	0·1	0·2
Starch (by acid hydrolysis)	71·6	70·3	78·2	78·4
Crude fibre..	1·9	2·2	0·2	0·3
Ash	1·7	1·9	0·5	0·4
Hydrocyanic acid.. ..	0·0006	0·0012	Nil	0·0008

The roots were thus of normal composition; also the starches, except that the percentages of actual starch were low. Gelatinisation tests showed sample (*d*) to be better than (*c*). A sample of a fine buff-coloured meal, described as "specially prepared starch from the refuse of starch previously made," would probably prove suitable only for such uses as the manufacture of cattle foods, and gelatinisation tests showed it to be much inferior to samples (*c*) and (*d*). D. G. H.

***Zamia Furfuracea* Starch from British Honduras.** (*Bull. Imp. Inst.*, 1934, **32**, 374–375.)—The starch examined was stated to have been prepared from the underground stems of *Zamia furfuracea*, a plant indigenous to British Honduras; it consisted of slightly granular starch of fair colour but gritty in the mouth. It contained:—Moisture, 14·6; crude proteins, 0·4; fat, 0·2; starch (by acid hydrolysis), 80·6; other carbohydrates (by diff.), 2·6; crude fibre, 0·2; and ash, 1·4 per cent. The ash contained a high proportion of silica, possibly owing to contamination during preparation. A gelatinisation test with 10 g. of Zamia starch and 100 ml. of water produced a jelly somewhat firmer than was yielded by St. Vincent arrowroot under similar conditions, but of rather inferior colour. D. G. H.

Fluosilicates and Wines. H. Fabre and E. Brémond. (*Ann. Falsif.*, 1934, **27**, 453–466.)—The proportion of fluorine regarded as normal in a wine is 5 mg. per litre. Any amount appreciably exceeding this may be due to either

(i) fraudulent addition of soluble fluoride with the object of masking or combating bacterial disease, or (ii) treatment of the vines, too late in the season, with insecticidal powders with a basis of barium or sodium fluosilicate. The second of these practices may result in delay or premature stoppage of the fermentation.

T. H. P.

Tests of the Suitability of Acetic Acid for Clinical Work. J. Hillen. (*Pharm. Weekblad*, 1934, **71**, 1210–1214.)—The benzidine test (*cf.* K. Serke, *Apoth. Zeit.*, 1929, 1018) is unreliable, as samples of acetic acid may give a yellow colour when this reagent is dissolved in them, and still be suitable for clinical work. It is suggested that (i) a solution of 10 mg. of benzidine in 5 ml. of the sample should be mixed with 2 ml. of 3 per cent. hydrogen peroxide; there should be no green colour after 5 minutes; (ii) a mixture of 1 ml. each of Schiff's reagent and of the sample is allowed to stand for 5 minutes, and 10 ml. of dilute sulphuric acid are added. A red or purple colour should not appear, although a blue colour is permissible.

J. G.

Stability of Mixtures of Hydrogen Peroxide and Ethyl Alcohol. W. A. Woodard and J. Pickles. (*Quart. J. Pharm.*, 1934, **7**, 418–421.)—Mixtures of ethyl alcohol and hydrogen peroxide (10 vol.) prescribed as ear-drops are frequently supplied ready-mixed, and have then been known to occasion stinging and irritation if used after a relatively long period. It is shown that about 1 per cent. of acetic acid and 0·44 per cent. of acetaldehyde may be produced after storage for 3 months at 60° to 65° F. in greenish-white bottles in a bright light, and that the *p*H value falls from 4·8 to 2·6. The residual peroxide-content is less than that of the corresponding solution of hydrogen peroxide stored separately. The constituents should therefore be dispensed separately in amber bottles and stored in a cool, dark place.

J. G.

Preparation and Properties of *Mentholum Valerianicum*. B. Bobranski. (*J. Pharm. Chim.*, 1934, **20**, 437–442.)—*Mentholum valerianicum* ("Validol"), which is a solution of menthol in menthyl isovalerate, should contain 66 to 73 per cent. of ester, corresponding with the saponification value 155 to 170. It may be prepared either by the action of isovaleryl chloride on menthol, or by the esterification of menthol with valeric acid, menthol being then dissolved in the product. The method with isovaleryl chloride gives good yields but a poor product, owing to impurities in the acid chloride, which is prepared by means of thionyl chloride or one of the phosphorus chlorides. The esterification process requires either sulphuric or gaseous hydrochloric acid as a catalyst. The former causes the formation of menthene and not menthyl isovalerate. The use of gaseous hydrochloric acid results in a product having an agreeable odour, and closely resembling "Validol." The isovaleric acid is mixed with about 18 per cent. of menthol in excess of the theoretical amount, and gaseous hydrochloric acid is passed through the mixture for an hour in the cold. The flask is then heated on the water-bath, beneath a reflux condenser, for seven hours, the acid gas still being bubbled through the mixture. After cooling, the product is washed twice with water, once with 5 per cent. sodium hydroxide solution, and once again with water, the same volume of wash liquid as of ester being used. The product is then dried with anhydrous potassium carbonate (2 g. for each 20 g. of menthol) and distilled at a pressure of 1·5 mm. of mercury. Natural menthol, B.P., gave a product having a boiling range, at 1·5 mm., of 80°–125° C.; synthetic menthol (Schimmel), 70°–115° C.; and another synthetic menthol (Schering), 65°–118° C. The optical rotations were:—Natural $[\alpha]_D^{21^\circ}$ −51·8°; synthetic (Schimmel), −20·40°; and synthetic (Schering), +1·3°. *l*-Menthyl isovalerate should have $[\alpha]_D^{21^\circ}$ −64·02° and saponification value 233. S. G. S.

Determination of Nicotine by the Silicotungstic Acid Method. N. H. Pizer. (*J. Soc. Chem. Ind.*, 1934, **53**, 356–357T.)—The application of this method to the determination of nicotine in concentrations of 0·01 per cent. or less has been investigated. Particular attention has been given to the temperature of ignition of the nicotine silicotungstate which must be such that all the carbon is burnt off and the silicic acid dehydrated, and no loss of tungsten trioxide occurs by volatilisation. The temperature 1000° C. fulfils these requirements. With the A.O.A.C. official method (*Methods of Analysis*, 1930, 55), and taking quantities of "pure" nicotine varying from 0·1 to 0·01 g., the percentages found lie between 99·63 and 100·20; with 0·005 g. of nicotine, 99·15 per cent. was obtained. T. H. P.

Colorimetric Determination of the Preservative Value of Hops. A. A. D. Comrie. (*J. Inst. Brewing*, 1934, **40**, 420–424.)—Earlier methods (*cf.* Guthrie and Philip, ANALYST, 1933, **58**, 411) have been improved as follows:—About 50 g. of the freshly-minced and mixed sample are shaken with 100 ml. of methylated spirit, and 1 ml. of the supernatant liquor is diluted to 50 ml. with methylated spirit in a graduated flask; this is stable for 24 hours. A mixture of A (usually 5) ml. of this extract and 1 ml. of a 1 per cent. solution of uranium nitrate in methylated spirit is matched in a colorimeter against a 10 per cent. solution of (A.R.) ferric chloride, every 100 ml. of which contains 1 ml. of N hydrochloric acid. The liquids are brought to the same level with methylated spirit, and the final match is obtained by adding to or removing from the ferric chloride standard and so varying the depth, the solutions being viewed vertically; the depth is measured (B mm.) and should fall within the range 40 to 70 mm. In order to calibrate the standard iron solution 0·0316 g. of the α-resin lead salt is prepared (*loc. cit.*) and ground with 5 ml. of methylated spirit and 0·4 ml. of 20 per cent. sulphuric acid until the lead salt has decomposed completely. It is then washed with methylated spirit into a separating-funnel containing 20 ml. of a 1 per cent. solution of common salt, and is extracted 4 times with 10 ml. portions of petroleum spirit (b.p. 38° to 40° C.), the extracts being filtered and evaporated first at 140° F., and finally, when 5 ml. remain, at 110° F. To a solution of the residue in methylated spirit are added 5 ml. of a 0·1 per cent. solution of bromothymol blue and sufficient of a 0·1 per cent. solution of xylene cyanol-*FF* to give a shade of green which matches that of a normal 10 per cent. hop extract, methylated spirit being the solvent in all cases. The mixture is diluted to 100 ml., and the depth of the ferric chloride solution (C mm.) required to give a colour which matches that of 4 ml. of the standard (≡ 0·8 mg. of α-resin) is determined. Then the preservative value is $16\,AB/C$. The methylated spirit for use is prepared by distillation of the industrial quality, the first 50 ml. being rejected and the last three-quarters of the total volume collected. The same supply should be used both for the standardisation and for the actual determination, and 10 ml. should show no turbidity for 1 hour after the addition of 1 ml. of a 1 per cent. solution of uranium nitrate; this test may be used to determine the end-point of the distillation. The graph given in the paper demonstrates the linear relationship between the α-resin present and *B*. The results obtained for 6 samples of English (1933) hops from different localities agree reasonably well with the gravimetric method of Hastings and Walker (*id.*, 1933, **58**, 702) for hops of good quality if the formula $10\ (\alpha+\beta/3{\cdot}0)$ is used to calculate the preservative value in the latter case. The poorer hops show wider divergencies, although not so great as that observed by Guthrie and Philip (*loc. cit.*) for a sample of old hops; these discrepancies may be due to differences in the source of light used, since Van Laer has shown that the light absorbed by the uranium compounds of the α- and β-resins varies throughout the spectrum. The method is not intended to replace the gravimetric procedure, but has the advantages of speed and simplicity. J. G.

Biochemical

Further Studies on the Availability of Iron in Biological Materials. W. C. Sherman, C. A. Elvehjem and E. B. Hart. (*J. Biol. Chem.*, 1934, **107**, 383–394.)—In previous papers (*J. Biol. Chem.*, 1933, **103**, 61; *J. Pediat.*, 1934, **4**, 65), the authors have shown that with sufficient copper, the iron of simple inorganic salts is used for haemoglobin regeneration in anaemic rats much more efficiently than the iron in the form in which it is found in a number of foods. The previous papers deal also with a method of determining the "available" iron present by the use of the α, α′-bipyridine reagent. The present paper deals with the availability of iron in liver, cardiac muscle, skeletal muscle, oysters, blood, soya beans, spinach and alfalfa. Beef and pork liver and cardiac muscle and soya beans have an availability of over 60 per cent., and beef skeletal muscle of 50 per cent., whilst that of oysters, spinach, alfalfa and blood is 25 per cent. or less. Results closely resembling those given by the bipyridine method were obtained by boiling the finely-ground, fresh material with 15 ml. of 5 *N* hydrochloric acid for 10 minutes in a 100-ml. beaker. The solution was then cooled and the protein was precipitated with 20 per cent. trichloroacetic acid; the precipitate was filtered off and washed with dilute trichloroacetic acid. The combined filtrates were then boiled with 0·25 ml. of 30 per cent. hydrogen peroxide and diluted to 50 ml. The iron in aliquot portions of this was determined by the thiocyanate and amyl alcohol extraction method. S. G. S.

Note on Bombicysterol. W. Bergmann. (*J. Biol. Chem.*, 1934, **107**, 527–532.)—The unsaponifiable fraction of the chrysalis oil of the silk moth, *Bombyx mori*, amounting to about 1·6 per cent. of the oil, contains, in addition to large amounts of hydrocarbons, 33 per cent. of cholesterol and 15 per cent. of sitosterols. The presence of bombicysterol was not detected. S. G. S.

Further Studies on the Concentration and Chemical Nature of Vitamin B_2 (*G*). L. E. Booher. (*J. Biol. Chem.*, 1934, **107**, 591–597.)—By the use of a specially prepared fuller's earth, vitamin B_2 has been concentrated from whey powder to between 200 and 300 times the original strength, the resulting product being an orange-red powder with an activity of between 3000 and 3500 Sherman units of B_2 per g. The author is of opinion that the water-soluble, yellow-green fluorescent pigment of whey is either the vitamin itself, or an integral part of it. Analyses of two separate batches gave: (i) C, 44·77; H, 6·87; N, 16·02; and (ii) C, 46·27; H, 7·46; N, 16·21; sulphur and phosphorus were absent.

S. G. S.

Investigation of the Growth-promoting Properties of Vitamin B_2 (*G*) Concentrates. L. E. Booher, H. M. Blodgett and J. W. Page. (*J. Biol. Chem.*, 1934, **107**, 599–605.)—A close correlation between the requirements for vitamin B_2 and the body-weights of growing animals has been established. This is responsible for certain ambiguities of interpretation of flattened growth-curves. When liberal quantities of highly active concentrates of vitamin B_1 and B_2 were fed to rats, growth was inappreciable, but an 80 per cent. alcoholic extract of whole wheat contained a factor (or factors) which supplemented these vitamins and promoted continuous growth. This new material in the wheat extract was relatively heat-stable, as compared with vitamin B_1, and was not dissolved by ether from the dried alcohol-extractives. S. G. S.

Toxicological

Extraction of Barbituric Acid Derivatives from Viscera by means of Acetone. P. Chéramy and R. Lobo. (*J. Pharm. Chim.*, 1934, **20**, 400–403.)—The use of acetone for extraction in the Stas–Otto–Ogier method has been found to simplify and accelerate the procedure. It causes the coagulation of protein and is a good solvent for barbiturates, but does not dissolve substances, such as lecithin, which form emulsions with other volatile solvents. The finely-divided viscera are placed in a flask, and a solution of tartaric acid (20 per cent.) is added until the reaction is definitely acid, when 2½ volumes of rectified acetone are added in small portions and with shaking. The flask, to which is affixed a reflux condenser, is heated for two hours on the water-bath. After cooling, the contents of the flask are collected on a filter which has been moistened with acetone. The flask is rinsed out twice with small portions of acetone, and finally the residue on the filter is pressed. The acetone solution is then distilled under reduced pressure, by the method described by Ogier and Kohn-Abrest (*Traité de Toxicologie*, Vol. II, p. 88), which prevents the formation of froth. The concentration is taken to the point at which the residue has the consistence of a soft extract, after which, it is re-dissolved, in the same flask, in 200 ml. of pure acetone. Solution is assisted by warming and by shaking with glass beads; a turbid liquid is always obtained. The contents of the flask are then cooled as rapidly as possible (preferably on ice) and collected on a small filter moistened with acetone, the flask being rinsed out with the same solvent. The filtrate is distilled at normal pressure, as there is no fear of frothing and the temperature is sufficiently low for no alteration of barbiturates to take place. The syrupy residue is then dissolved in 200 ml. of water, 20 to 30 g. of ammonium sulphate are added, and the solution is warmed to drive off the last traces of acetone. It is then rapidly cooled and collected on a moistened filter, the filter and flask being washed with a small amount of 10 per cent. ammonium sulphate solution. The filtrate, which must be definitely acid, is shaken three times with half its volume of ether. The combined ethereal extracts are washed with a small amount of water and, after being dried with anhydrous sodium sulphate, are distilled on the water-bath. The residue, which corresponds with the "acid ether extract" of the Stas-Otto method, contains the barbiturates. With organs containing large amounts of lipins, the residue from the first acetone extraction is dissolved in 200 ml. of warm water and 20 g. of ammonium sulphate are added. This solution is then cooled and filtered. The filtrate and wash-liquids are distilled under reduced pressure, and the residue is dissolved in 200 ml. of anhydrous acetone and treated as before (second acetone extraction). If the final product of the extraction is coloured, it is re-dissolved in water, the solution is treated with a little decolorising charcoal (Norit), then warmed and filtered, and the residue is washed with warm water. The aqueous solution is then acidified with hydrochloric acid and extracted with ether. S. G. S.

Identification of Barbiturates in Urine. M. Fauchet. (*J. Pharm. Chim.*, 1934, **20**, 403–406.)—The urine is treated with one-tenth of its volume of neutral lead acetate solution and filtered, the filtrate is acidified and extracted with half its volume of ether or, preferably, ethyl acetate, and the ethereal extracts are mixed and washed twice with half their volume of water. The barbiturates, now in the ethereal solution, can be quantitatively extracted by means of 4 per cent. ammonia solution; by this method they can be obtained in an alkaline solution, which can then be concentrated to a small volume on the water-bath. Several ml. of the liquid under examination are treated in a centrifuge tube with 2 ml. of a copper-pyridine reagent. (This is prepared by adding pyridine in slight excess to a 3 per cent. solution of copper sulphate until the precipitated hydroxide re-dissolves and then centrifuging the liquid to obtain a clear product.) A characteristic violet precipitate is formed and can be separated from the mixed solutions by centrifuging (the supernatant liquid should still be blue). The precipitate is washed (not more than twice) with a little water, collected, and dried on a small filter-paper. This is sufficient to establish the fact that a barbiturate has been ingested, but confirmation may be obtained by submitting the violet precipitate (previously dried on the water-bath) to micro-sublimation in a tube, 3 to 4 cm. long and 0·005 cm. diameter, which is heated in a Bunsen flame. The copper-pyridine-barbiturate decomposes, and the barbiturate sublimes. The sublimate can then be compared with known substances. Alternatively, the violet precipitate may be treated with a drop of 10 per cent. sulphuric acid on a microscope slide, and the crystals so formed compared with those obtained under similar conditions from known substances. Allyl derivatives of barbituric acid (*e.g.* dial) are not usually found in the urine, as they are decomposed in the body;

the newer preparations, having a substituted methyl group attached to one of the nitrogen atoms (*e.g.* prominal and evipan), which are used in the form of a sodium salt, do not give the violet precipitate with the copper-pyridine reagent.

S. G. S.

Rapid Method for the Identification of Barbiturates in Blood. P. Chéramy and R. Lobo. (*J. Pharm. Chim.*, 1934, 20, 461–462.)—Persons suffering from barbiturate poisoning bleed easily, and the blood samples may be examined rapidly by a modification of the acetone method previously described (*supra*). Fifty ml. of blood are taken, and as this has usually coagulated, the serum is poured into a flask, and the clot is triturated in a mortar with its own volume of washed sand. This is then stirred with small portions of pure acetone, which is decanted into the flask containing the serum. The flask must be shaken so that a flocculent precipitate of the proteins may be formed. Finally, the contents of the mortar are transferred to the flask by means of acetone with the aid of a spatula, the total volume of acetone being at least four times that of the blood taken. A solution of tartaric acid (20 per cent.) is then added until the reaction is definitely acid, when the flask is attached to a reflux condenser and boiled for 20 to 30 minutes on the water-bath. The flask is then cooled rapidly in ice-water, and the contents are collected on a filter which has been wetted with acetone, and the filter is washed with a little acetone and carefully pressed. The acetone solution is distilled in a fairly large flask (to avoid frothing) on a water-bath at normal pressure. The contents of the flask are then transferred to a dish, and the rest of the acetone is evaporated in the open air. The aqueous residue is treated in the dish with a solution of ammonium sulphate such that the final volume is 100 ml. and contains 15 g. of ammonium sulphate. Heating on the water-bath is continued for several minutes, after which the dish is cooled in ice-water and its contents are collected on a filter which has been moistened with ammonium sulphate solution, and washed with a little ammonium sulphate solution. The filtrate and washings, which must be acid, are extracted three times with half their volume of ether. The mixed ethereal solution is washed with a little water, dried with anhydrous sodium sulphate, and evaporated to dryness in a tared crystallising dish. The presence of a crystalline residue indicates a barbiturate, which may be identified by the usual reactions. S. G. S.

Agricultural

Determination of Magnesium in Extracts of Soil in Hydrochloric Acid by the Oxine Method. H. J. Hardon and W. Wirjodihardjo. (*Chem. Weekblad*, 1934, 31, 662.)—Ten ml. of an extract of 55 g. of soil in 125 ml. of cold 25 per cent. hydrochloric acid are heated with 1 ml. of concentrated nitric acid, and when red fumes are no longer evolved, the solution is cooled and 100 ml. of 20 per cent. sodium tartrate solution, 100 ml. of *N* sodium hydroxide solution, and then 20 ml. (a drop at a time) of a 2 per cent. solution of oxine in alcohol are added; the *p*H value should be about 11·5 (*cf.* Fleck and Ward, ANALYST, 1933, 58, 388). The solution is heated at 70° C. and stirred well to cause flocculation of the precipitate, which is removed by filtration and washed with a 2 per cent. alkaline solution of sodium tartrate until the filtrate is colourless. It is then dissolved in 10 per cent. hydrochloric acid, 10 drops of concentrated sulphuric acid are added, and the solution is evaporated, the residue being re-dissolved in 25 per cent. hydrochloric acid. Manganese is precipitated by adding 10 ml. of 10 per cent. ammonium chloride solution, bromine water and ammonia and warming; if the manganese-content is high, re-precipitation is desirable. Calcium is next precipitated with ammonium oxalate and ammonia, and, after 1 hour on the water-bath, the liquid is boiled with 10 ml. of 25 per cent. ammonia, and excess of a 2 per cent. solution of oxine in alcohol is added. After 30 minutes on the water-bath the precipitate is filtered off, washed with 2·5 per cent. ammonia, and dissolved in 10 ml. of warm 10 per cent. hydrochloric acid, and the solution is titrated with $N/10$ potassium bromate solution in the presence of 5 ml. of 10 per cent. potassium bromide solution, with methyl red as indicator. The extreme errors for extracts of soils containing 5·55 to 24·01 mg. of magnesium per 10 ml. and varying quantities of iron, aluminium, manganese and calcium, were — 0·18 to + 0·24 mg. J. G.

Organic

Determination of Copper in Organic Compounds. N. N. Melnikow. (*Z. anal. Chem.*, 1934, **99**, 182–184.)—The compound (0·1 to 0·5 g.) is treated exactly as described for the determination of thallium (ANALYST, 1934, **59**, 843) to the point where the excess of permanganate has been removed. The solution is cooled, diluted to 200 ml., treated with 0·5 g. of potassium iodide and 20 to 25 ml. of 10 per cent. potassium thiocyanate solution, and titrated with 0·02 N thiosulphate solution, with or without starch indicator. W. R. S.

Identification of Metanilic and Sulphanilic Acids. R. B. Forster. (*J. Soc. Chem. Ind.*, 1934, **53**, 358T.)—These acids may be identified by converting them, by the Gattermann reaction, into the corresponding chlorobenzenesulphonic acids, acting on these with phosphorus pentachloride to form the chlorobenzenesulphonyl chlorides, and then preparing the chlorobenzenesulphonamides, which are characterised by their melting-points. The properties of various arylamine salts of the two chlorobenzenesulphonic acids are given. It has been shown that naphthylaminemonosulphonic acids may be identified by means of suitable arylamine salts of their acetyl derivatives (Forster and Watson, *ibid.*, 1927, **46**, 224T), but attempts to form similar salts of metanilic and sulphanilic acids failed, owing to the ease with which their acetyl derivatives are hydrolysed. If, however, the amino-group of the acids is replaced by chlorine, the resulting chloro-compounds readily yield arylamine salts, some of which are easily purified and melt sharply. T. H. P.

Inorganic

New Test for Mercury. E. Stathis. (*Z. anal. Chem.*, 1934, **99**, 106–108.)—One ml. of the solution to be tested is treated with 0·5 ml. of 1 per cent. potassium iodide solution, 1 ml. of 20 per cent. potassium hydroxide solution and 5 ml. of 0·01 per cent. gold chloride solution. If mercury is present, a violet colour is immediately produced, owing to the formation of colloidal gold. In the detection of minute amounts of mercury, a blank test is made; this shows a faint reddish tinge after about 5 minutes. W. R. S.

Study of Dotreppe's Method for the Determination of Tungsten. M. L. Holt. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 476.)—The author has studied Dotreppe's method (*Chim. et Ind.*, Special No. 173–8, March, 1931), which involves reduction of tungstate by zinc and hydrochloric acid in an atmosphere of carbon dioxide and subsequent titration with the aid of ferric alum and permanganate, the calculation being based on an apparent reduction of WO_3 to W_4O_7. He has found that the reduction was incomplete and variable, and that consistent results could not be obtained, and therefore concludes that the method is unsatisfactory. S. G. C.

Volumetric Determination of Nickel and Cobalt. J. T. Dobbins and J. P. Sanders. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 459–460.)—The solution (150 ml.), containing 0·05 to 0·1 g. of cobalt or nickel, is rendered just acid to litmus with nitric acid, and 3 ml. of pyridine and an excess of standard ammonium thiocyanate solution ($N/10$) are added, with the result that the metals are precipitated in a filterable form as the complex pyridine thiocyanates. The liquid is diluted to 250 ml. and filtered. A 50-ml. portion of the filtrate is diluted to 100 ml., 1 ml. of concentrated nitric acid is added, and an excess of standard silver nitrate solution ($N/10$) is added to precipitate the ammonium thiocyanate in solution. The excess of silver nitrate is titrated with standard ammonium thiocyanate, ferric alum being used as indicator. The calculation of the result is based on the reaction of 1 atom of the metal with 2 molecules of thiocyanate to form an insoluble compound of the general formula $MPy_4(SCN)_2$. The results of test-titrations carried out with solutions of cobalt and nickel salts were in close agreement with those obtained by the electrolytic method for cobalt and the dimethylglyoxime method for nickel. When cobalt and nickel are present together, the total quantity may be determined as outlined above, and, if the nickel is determined separately by the dimethylglyoxime method, the cobalt may be obtained by difference. S. G. C.

Use of *Cyclo*hexanol in the Colorimetric Determination of Molybdenum. L. C. Hurd and F. Reynolds. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 477–478.)—*Cyclo*hexanol is claimed to be superior to ether or ether mixtures as solvent for extracting the red molybdenum thiocyanate from aqueous solution, since in *cyclo*hexanol the coloured compound is more stable and more soluble; the lower volatility of *cyclo*hexanol is also regarded as an advantage. In tests carried out on a range of steels and molybdenum alloys, the ether extraction method (*cf.* James, *id.*, 1932, **4**, 89; King, *Ind. Eng. Chem.*, 1923, **15**, 350) gave errors of 0 to 10 per cent., whilst, with the use of *cyclo*hexanol, the maximum error was 5·5 per cent. S. G. C.

Determination of Tellurium in Tellurium-Lead Alloys. W. J. Brown. (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 428–429.)—I. *Tellurium Lead.*—A 12·5-g. sample of the alloy sawings is dissolved in 100 ml. of dilute nitric acid (1 : 4) by heating on a water-bath; 25 ml. of sulphuric acid (1 : 1) are added, the liquid is cooled, diluted to 500 ml. and filtered, and 400 ml. of the filtrate are taken. This is evaporated until fumes of sulphuric acid are given off, and, after cooling, the residue is diluted to 50 ml., 5 g. of tartaric acid are added, and the solution is boiled, cooled, kept for 2 hours and filtered; the residue is washed and discarded. The tellurium, copper, bismuth, etc., in the liquid are precipitated by saturating it with hydrogen sulphide, and the precipitate is ultimately filtered off and washed with hydrogen sulphide water. The precipitate is returned to the precipitating vessel with the minimum quantity of water; a few g. of sodium bicarbonate and 5 ml. of sodium sulphide solution (10 per cent.) are added, and the liquid is warmed for some time. This procedure causes most of the tellurium disulphide in the precipitate to dissolve, but leaves a little entrapped in it. The solution is filtered and the residue is reserved (see below). The filtrate is acidified with sulphuric acid, the tellurium is precipitated with hydrogen sulphide, and the precipitate is filtered off, washed, and returned to the beaker with the minimum quantity of water. The tellurium sulphide is dissolved by adding an equal volume of concentrated hydrochloric acid and 1 g. of potassium chlorate, and heating to boiling; any residue is filtered off and rejected. The solution is evaporated to dryness on a water-bath after the addition of a few ml. of nitric acid. The residue is dissolved in 100 ml. of hydrochloric acid (9 : 1), and a few g. of tartaric acid are added; the solution is heated to boiling, and sulphur dioxide is passed into it for 5 minutes; then 100 ml. of boiling water are added, and the passage of sulphur dioxide is continued for 30 minutes. The liquid is kept for 1 hour in a warm place, sulphur dioxide is again passed for 20 minutes, and the precipitate of elemental tellurium is filtered off on a Gooch crucible, washed with hot water and finally with alcohol, dried at 100° C. for 1 hour, and weighed. "Treat the residue held in reserve (above) with hot hydrochloric acid to which potassium chlorate has been added, and proceed as described above. The final precipitate of tellurium may be filtered separately or combined with the main portion." II. *Antimonial Tellurium Lead* (containing up to 10 per cent. of antimony).—A 10-g. sample of the alloy sawings is dissolved, so far as possible, by heating with 175 ml. of "bearing metal solution" (a mixture of 400 ml. of concentrated hydrochloric acid, 200 ml. of concentrated nitric acid, 40 g. of potassium chloride and 1000 ml. of water). The solution is decanted from the residue and the crystalline mass of lead chloride. A further 175-ml. quantity of the "bearing metal solution" is added to the residue, and the whole is heated until complete solution is secured. Both solutions are cooled and kept overnight; the lead chloride is filtered off, washed with cold dilute hydrochloric acid (1 : 1), and rejected. The combined filtrates are evaporated to dryness on a water-bath. The residue is dissolved in 100 ml. of hydrochloric acid (9 : 1) and heated to boiling; sulphur dioxide is passed into the liquid for 1 hour, 100 ml. of boiling water being added after the first 30 minutes. The liquid is kept in a warm place for 1 hour, and sulphur dioxide is again passed for 20 minutes. The precipitate of tellurium is filtered off on an asbestos filter and washed a few times with dilute hydrochloric acid (1 : 2), and finally with water. The filter and precipitate are heated with a mixture of 10 ml. of concentrated nitric acid and 10 ml. of concentrated sulphuric acid until the precipitate is dissolved, and the liquid is diluted and filtered. The filtrate is evaporated until fumes of sulphuric acid are given off; the residue is diluted to 50 ml., 5 g. of tartaric acid are added, and the solution is heated to boiling. The liquid is cooled and kept for 1 to 2 hours, when any precipitate which has formed is filtered off and discarded. The solution is treated further as in I. In test experiments, 0·01 g. quantities of tellurium were recovered from admixture with 12·5 g. of lead or 10 g. of antimonial lead, 0·005 g. of copper and 0·005 g. of bismuth, the maximum errors being +0·0003 g. and −0·0004 g. S. G. C.

Microchemical

Spot Tests for Organic Compounds. I. F. Feigl. (*Mikrochem.*, 1934, **15**, 1–8.)—*Identification of atomic groupings* $>C=S$ and $\gg C\text{–}SH$.—The reaction $2NaN_3+I_2=2NaI+3N_2$ proceeds very slowly, but is catalysed by traces of divalent sulphur compounds such as sulphides and thiocyanates. Organic sulphur compounds containing the groups $>C=S$ and $\gg C-SH$ also catalyse the reaction, but other sulphur compounds, *e.g.* *R*–S–*R*, *R*–S–S–*R*, *R*–SO$_2$–*R*, *R*–SO$_2$H and *R*–SO$_3$H and their salts, are without effect. The test is carried out on a watch-glass, a drop of the organic sulphur compound in solution in water or an organic solvent (not carbon disulphide) being mixed with a drop of the iodine and azide reagent, and any evolution of minute bubbles of nitrogen noted. The substance can also be tested in the solid or liquid form after evaporation of the solvent, when even smaller amounts can be detected. The reagent is prepared by dissolving 3 g. of sodium azide in 100 ml. of $N/10$ iodine solution, and will keep for some months. A table of the 25 compounds tested is given, together with the limit of identification and the limit concentration, and the solvent used in each case. The limit of identification ranges from 2·5γ to 0·0003γ, and the concentration limit from 1:10,000 to 1:10,000,000. The test is most sensitive for thioacetic acid.

Sulphur dyestuffs.—The behaviour of the sulphur dyestuffs in the iodine and azide test indicates differences in constitution. The following were examined:—(i) Primuline yellow: no reaction; (ii) Katigen brown extra: vigorous development of nitrogen; (iii) Katigen brilliant green: development of nitrogen; (iv) Katigen yellow 66, extra: very vigorous development of nitrogen; (v) Katigen black: S.W., extra: very vigorous development of nitrogen; (vi) Katigen indigo C.L. extra: very vigorous development; (vii) Katigen violet 3K: very vigorous development. As primuline yellow contains only the thio-ether group, a positive reaction was not to be expected. A thread of material dyed with the dyestuff under examination may be used for the test.

III. *Differentiation between animal and vegetable fibres by means of the azide and iodine reaction.*—Animal fibres contain protein, in which the cysteine sulphur gives the reaction with azide and iodine, whilst vegetable fibres do not react. The thread to be tested is placed on a watch-glass and moistened with a drop of water or acetone, and one or two drops of the reagent are added. After a short time the thread (if animal) is covered with minute bubbles. Cotton fibres are coloured violet by the iodine, but the colour of wool fibres remains unchanged. Both bleached and unbleached cotton give the violet colour, but bubbles are not formed in either case. J. W. M.

Spot Tests for Organic Compounds. II. F. Feigl, V. Anger and O. Frehden. (*Mikrochem.*, 1934, 15, 8–22.)—*Detection of Carboxylic acids and their derivatives* (anhydrides, esters, halogenides).—The so-called hydroxamic acids, R–CO(NHOH), react in acid solution with ferric chloride to give a red or violet colour, through the interaction of the acid CO(CNOH)– group and the ferric ion to form an inner complex salt. Hydroxamic acids are easily prepared from the carboxylic acid anhydrides, esters, amides and halogenides by treatment with hydroxylamine and addition of alkali; the reaction is rapid and can be carried out on the micro-scale. Free carboxylic acids must first be converted into the acid chlorides by treatment with thionyl chloride. *Methods.*—(i) *Carboxylic acid anhydrides.*—The anhydride is dissolved in ether, and a drop of the solution is placed in a micro-crucible, together with a drop of the reagent solution (an approximately 0·5 per cent. solution of ferric chloride, acidified with a little concentrated hydrochloric acid, and then saturated with hydroxylamine hydrochloride). The mixture is evaporated to dryness, and a few drops of water are added. In the presence of an anhydride, a violet, lilac or rose colour develops, according to the amount present; the blank test remains colourless. (Alternatively, this reaction may be used as a test for hydroxylamine.) A table is given of eight different acid anhydrides, together with the limit of identification and colour produced in each case. The limit of identification varies between 5γ and 10γ. (ii) *Carboxylic acid esters.*—A drop of the ethereal ester solution is treated in a micro-crucible with a drop of a saturated alcoholic solution of hydroxylamine hydrochloride and a drop of saturated alcoholic alkali, and warmed gently until the reaction begins. A drop of alcoholic hydrochloric acid is added and, finally, a drop of a very dilute aqueous solution of ferric chloride; a brown-red to blue-violet colour indicates the presence of the ester. The blank test shows only the pale yellow colour of the ferric chloride. All esters react, including lactones, and orthocarboxylic esters and thiocarboxylic acid esters give orange or red colours, and in one instance a dark green colour. Formic acid, which gives a red colour under the same conditions, must not be present. A table is given of 50 esters, together with the description of the colour and the limit of identification in each case; this ranges from 1 to 13γ. (iii) *Carboxylic acid chlorides.*—A drop of the ethereal solution of the acid chloride is treated on a spot plate or in a micro-crucible with a sodium hydroxide hydroxylamine solution, acidified with hydrochloric acid, and, finally, a drop of a dilute aqueous solution of ferric chloride is added. A brown-red to violet colour indicates the presence of the acid chloride. (iv) *Carboxylic acids.*—A drop of the solution of the acid is evaporated to dryness, or the test is carried out on a granule of the solid substance, both in a crucible; 10 drops of thionyl chloride are added, and the mixture is evaporated almost to dryness, whereby the acid is converted into chloride. Two drops of a saturated alcoholic solution of hydroxylamine hydrochloride and a few drops of alcoholic alkali to render the mixture alkaline are added, and, after being heated, the mixture is acidified with a few drops of hydrochloric acid, followed by the dilute ferric chloride solution. A table is given showing the colour formed and the limit of identification for the test with 20 different acids. The range of identification limit is from 11γ to 100γ, the test being least sensitive for sodium acetate. (v) *Use of the ester test for* *technical samples.*—The method is used for various tests of purity of oils and fats, such as the detection of fat present as an impurity in medicinal vaseline, or in any mineral oils (which give a negative reaction). The 38 different oils, fats and waxes tested gave a positive reaction, the colours ranging from violet to violet-red and violet-brown or greenish-brown (yellow beeswax, refined lard). J. W. M.

Detection of Coumarin. A. Kofler and J. Geyr. (*Mikrochem.*, 1934, **15**, 67–73.)—For the identification of coumarin in plant material, micro-sublimation alone does not afford sufficiently characteristic crystals to be conclusive, and even the van Zijp (*Pharm. Weekbl.*, 1927, **64**, 841) reaction with mercuric iodide carried out on the sublimate is not always satisfactory, as many other substances give coloured addition compounds with iodine. If, however, the m.p. of the crystalline sublimate is determined on the cover-slip by means of the Kofler and Hilbck micro-melting-point apparatus (*Mikrochem.*, 1931, **9**, 38; Abst., ANALYST, 1932, **57**, 130) with either a thermometer or a thermo-electric couple, identification is certain. There are two modifications of coumarin, the stable form of which is in rhombic hemimorphous crystals, with positive optical character, and with angle $2V=80°$; it melts under the microscope at 67° C. The meta-stable form is monoclinic, has negative optical properties with a small crystal angle, and melts at 64° C. The micro-sublimate of *Herba herniariae*, contrary to recorded statements, was found to be not coumarin, but methyl-umbelliferone. J. W. M.

Microchemistry of Diethyl Bromoacetyl Urea (Adaline). M. Wagenaar. (*Pharm. Weekblad*, 1934, **71**, 1261–1264.)—Adaline, $(CH_3CH_2)_2.CBr.CO.NH.CONH_2$, is a colourless and odourless micro-crystalline powder, m.p. 116 to 118° C., with a slightly bitter taste. It sublimes in droplets or in micro-crystals which, when moistened with acetone, form identifiable crystals, and provide a test sensitive to 1 mg. If a suspension of a crystal in a drop of water is mixed with a drop of acetone or of chloral hydrate, and the solvents are removed by evaporation (*cf.* C. Génot, *Chim. et Ind.*, 1925, II, 679), feathery tufts of needles are obtained (sensitiveness 0·5 mg.). When a solution of a crystal in concentrated sulphuric or nitric acid is diluted considerably, needle- and star-shaped complex crystalline forms result, which resemble those obtained from acetone-water (*supra*); rectangles also occur, and the crystals show interference colours with crossed Nicol prisms (sensitiveness 0·1 mg.). The bromine atom in adaline reacts with silver nitrate, and a solution of the resulting silver bromide in ammonia yields characteristic rectangles on evaporation. Similarly, the action of warm platinum sulphate acidified with sulphuric acid produces octahedra of ammonium platinum bromide, and, on addition of a crystal of potassium bisulphate, well-defined octahedra of potassium platinum bromide result (sensitiveness 0·5 mg.). J. G.

Detection of Zinc by Induced Precipitation. P. Krumholz and J. Vazquez Sanchez. (*Mikrochem.*, 1934, **15**, 114–118.)—Cobalt salts give with alkali mercuri-thiocyanates a crystalline precipitate of the blue cobalt salt: $Co[Hg(CNS)_4]$. The precipitation takes place very slowly and incompletely in dilute solutions; if, however, even a trace of the white zinc salt $Zn[Hg(CNS)_4]$ is also precipitated in the solution, the whole of the cobalt is brought down, and the blue colour of the precipitate enables the zinc to be identified. *Detail.*—The neutral or slightly acid (with mineral acid) test solution is mixed with an equal volume (about 1 ml.) of the cobalt solution (containing 0·02 per cent. of cobalt, in *N*/2 hydrochloric acid) and of the reagent solution (made by dissolving 8 g. of mercuric chloride and 9 g. of ammonium thiocyanate in 100 ml. of water and allowing the solution to stand for 3 or 4 days). After 3 minutes the mixture is shaken with 1 or 2 ml. of ether. In the presence of zinc a blue precipitate appears at once on the layer between the two liquids, the depth of colour depending upon the amount of zinc. In the absence of zinc the precipitate is apparent only after 4 or 5 minutes. The sensitivity of the test varies with the acidity; in neutral solution the *detection limit is* 2γ and *concentration limit,* 1 : 500,000; in *N*/10 hydrochloric acid the *detection limit* is 5γ, and *concentration limit,* 1 : 200,000. The test can also be carried out as a "spot" test, when 1 drop of the test solution and 1 drop of the cobalt solution are mixed on a "spot" plate or in a micro-crucible with a drop of the reagent and "scratched" for about 15 seconds with a glass rod. With a rapidity depending on the amount of zinc present, and at all events within 2 minutes, a blue precipitate appears. In the absence of zinc the precipitation is first apparent after 2 to 3 minutes. A blank test should be made. In neutral solution:—*Detection limit,* $0{\cdot}2\gamma$; *concentration limit,* 1 : 250,000; in *N*/2 hydrochloric acid:—*Detection limit,* $0{\cdot}5\gamma$; *concentration limit,* 1 : 100,000. The following table shows the sensitivity of the test in the presence of the limiting proportions of various other substances, 1 ml. of the various solutions being used:

Substance	Detection limit in γ zinc		Proportion limit	
	Neutral	*N*/2 HCl	Neutral	*N*/2 HCl
Ammonium chloride	5	10	1:1000	1:500
Potassium sulphate	5	10	1:2000	1:1000
Aluminium chloride	5	10	1:700	1:700
Chromium nitrate	5	5	1:200	1:100
Manganese sulphate	10	10	1:50	1:50
Ferric chloride	10	10	1:60	1:60
Cadmium chloride	10	10	1:200	1:100
Lead nitrate	10	10	1:500	1:300

When carried out as a "spot" test the following values were obtained:

Substance	Detection limit in γ zinc		Proportion limit	
	Neutral	*N*/2 HCl	Neutral	*N*/2 HCl
Ammonium chloride	2	2	1:250	1:250
Potassium sulphate	0·5	1	1:1000	1:500
Aluminium chloride	0·5	1	1:700	1:350
Chromium nitrate	0·5	0·5	1:100	1:100
Manganese sulphate	2	2	1:100	1:100
Ferric chloride	2	2	1:120	1:120
Cadmium chloride	2	2	1:200	1:200
Lead nitrate	1	2	1:500	1:250

J. W. M.

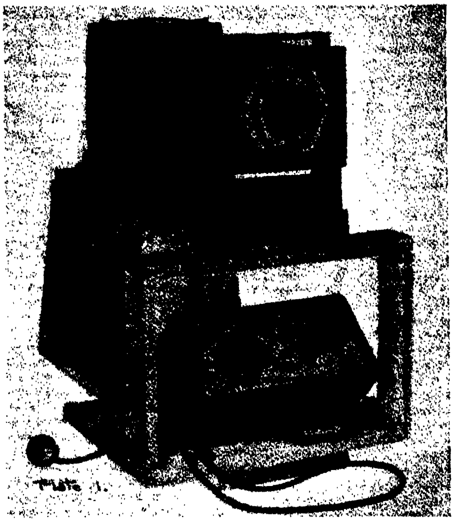
Spot Test for Hydrogen Peroxide. E. Plank. (*Z. anal. Chem.*, 1934, **99**, 105–106.)—Cerous sulphate solution is treated with strong potassium carbonate solution until the white precipitate redissolves. One to two drops of this solution are mixed on a spot-plate with the solution to be tested. Hydrogen peroxide produces a yellow to reddish-brown colour, due to potassium perceric carbonate. The reagent should always be freshly prepared. The test detects 0·001 mg. of hydrogen peroxide. W. R. S.

Physical Methods, Apparatus, Etc.

Spectroscopic Detection of Argon in Argon-Nitrogen Mixtures. J. A. M. Van Liempt and S. H. R. Visser. (*Rec. Trav. Chim. Pays-Bas*, **1934**, **53**, 1084–1086.)—In the usual Ruhmkorff method, or with a high-voltage, high-frequency alternating-current discharge (*e.g.* 300 kilocycles per second), the intensity of the nitrogen spectrum renders the argon lines visible only with difficulty; this applies even if the lengthy process of removal of most of the nitrogen by means of lithium or magnesium is first applied. The apparatus described is applicable to gas-filled lamps, which are connected by means of a special joint with a diffusion-pump, so that the gases can be transferred to a discharge-tube fitted with platinum electrodes at a pressure of 2 cm., the effect of the mercury lines being eliminated by interposition of a U-tube cooled in liquid oxygen or nitrogen. In this way it is possible to isolate the rings of the glow-discharge close to the upper electrode, and by observing, in particular, the line 415·9 $m\mu$, the effect of the argon spectrum is enhanced, as compared with that of the nitrogen. The method may be made quantitative. J. G.

Use of Ultra-Violet Light as a Sensitive Method for the Measurement of the Degree of Water-Resistance of Paper. J. Grant. (*J. Soc. Chem. Ind.*, 1934, **53**, 349–350T.)—The author's method for the identification of imitation water-marks (ANALYST, 1934, **59**, 749) is used. The mixture of rhodamine-6G and sugar is sprinkled on a piece of the specimen (about 2 inches square), which is then floated on the surface of distilled water at 21° ± 0·5° C., the time being noted with a stop-watch. The float described in the tentative standard method of the Technical Association of the Pulp and Paper Industry of America (*Tech. Assoc. Papers*, 1925, **8**, 91; P. W. Codwise, *id.*, 1932, **15**, 234) is convenient and prevents curling. The dry upper surface of the paper is observed in a dark room in filtered ultra-violet light, and the first sign of penetration is indicated by the almost instantaneous appearance on a dark background of the bright golden fluorescence resulting from the solution of the dye. The time is then again noted. The method overcomes the defects of the numerous other methods suggested (*cf.* F. T. Carson, *Tech. Papers Bur. Standards*, 1926, **20**, 703). The error, judged by the variation in consecutive readings, is less than 5 per cent., as compared with 15 per cent. for the ferric tannate test and 10 per cent. for the American dry-indicator test (*loc. cit.*). This increased accuracy is due to the smaller penetration times (about 60 per cent. of those obtained by the ferric tannate test), and to the extremely sharp end-points. It is advisable to test 10 specimens, *i.e.* 5 places on each side of the paper. J. G.

Ultra-Violet Light Source for Documentary Photography. L. Bendikson (*Library J.*, 15th Sept., 1934.)—A discharge coil or spiral of quartz-tubing (diameter 0·25 in.), sealed at both ends, and containing a mixture of helium, argon and mercury vapour at a very low pressure encircles the lens of the camera two or three times. Behind it is a metal reflector with a chequered surface encased in a square, black-lacquered housing (7 × 7 × 2½ in.), through which projects a cylinder (diameter 2½ in.), the front edge of the housing being provided with rims to take filters. Since the lens of the camera protrudes through the cylinder, the object is illuminated uniformly, so that shadows due to wrinkles or folds are minimised. Other advantages claimed are that the apparatus is cheap, and that very little heat is radiated, with the result that there is no danger of injuring the object to be photographed; 70 per cent. of the ultra-radiation has a wave-length between 254 and 257 $m\mu$ (18 per cent. at about 290$m\mu$); only short exposures are required. The illustration shows the camera on its base, with a portable adjustable transformer of the type used in therapeutic work, and in the background, a Corning filter cut to fit the front of the housing. Illustrations are provided of a palimpsest, of ink-eradication, a spurious bank-note and of a message in invisible ink, which was developed 150 years ago, but which has since faded (cf. *ibid.*, 1932, **57**, 784.)



J. G.

Reviews

HANDBUCH DER BIOLOGISCHEN ARBEITSMETHODEN. Edited by Professor EMIL ABDERHALDEN. Abteilung IV, "Angewandte chemische und physikalische Methoden"; Teil 13, "Quantitative Stoffwechseluntersuchungen"; Heft 5; Lieferung 412. Pp. 182, 48 illustrations. Berlin and Vienna: Urban and Schwarzenberg. Price RM. 8.60.

This number of Professor Abderhalden's enormous encyclopaedia comprises four expert contributions on the technique of experiments dealing with the chemical processes of respiration. From the point of view of the analytical chemist, the main items of interest are the determination of gaseous carbon dioxide and oxygen.

The first article, by Dr. F. Dickens (London) and Dr. F. Šimer (Bratislava), describes clearly and systematically the determination, by the phosphate and the bicarbonate methods, of the respiratory quotients in severed portions of living tissue. Both these processes involve interesting small-scale technique with the Warburg manometer—a technique which should have some application to general gas-volumetric methods. The second article, by Professor F. G. Benedict (Boston), is a detailed description of the design and use of the various types of helmet respiration apparatus; considerable space is given to the interesting "Rotameter" type of flow-meter. Dr. E. Simonsen (Frankfurt) and Dr. H. Hebestreit (Dresden) contribute an article of 67 pages on the use of the Simonsen respiration apparatus. The latter part of this article describes some interesting modifications of the Haldane gas-analysis apparatus; a feature of these is that the levelling-marks above the absorption pipettes are made movable, so that by adjustment of these the volume of gas sample taken originally in the measuring burette can be made exactly the same each time, calculation being thus facilitated. The reviewer agrees with the authors' preference for the use of small samples (10 ml.) as being much more convenient to work with than larger samples, and involving little or no loss in accuracy. A feature which might find other applications, *mutatis mutandis*, in routine analysis is the simultaneous manipulation of two instruments, one of which determines carbon dioxide only, and the other, carbon dioxide *plus* oxygen. The abolition of the Haldane compensator, even taking into account the greatly enlarged water jacket (17 litres) and the short time of working, seems rather a retrograde step. Professor T. M. Carpenter (Boston) contributes a very full description of his latest modification of the Haldane apparatus; the chief characteristic of this is a special absorption-vessel for oxygen, in which the pyrogallol solution is mechanically circulated. By this means, the oxygen determination, which is always the limiting time-factor in air analysis, is greatly accelerated. A modification for the determination of methane by combustion in a platinum-filled capillary is also described; a table of results of analyses by two different observers shows a definite personal factor which is, however, so small as to be of negligible importance. Figures of this kind are a valuable guide to analysts and assure confidence in a method. The only criticism to make of this article is that it fails to discuss the much-debated question of the extent of the evolution of carbon monoxide from pyrogallol. It is obvious from the figures given for the analysis of air that, with the apparatus and procedure described, the effect is negligible. In view, however, of the abundant evidence that in some circumstances it can cause serious error in air analyses, the subject ought to have been dealt with in an article of such length, which describes analyses of such high accuracy.

What faults there are in the publication as a whole seem to be due to insufficient editorial planning, rather than to any shortcomings in the contributions, the writers of which have, presumably, given only what they have been asked to give. Space which might have been more usefully filled is wasted by overlapping, as, for example, in the descriptions of (different) modifications of the Haldane apparatus in two of the articles. Some cross-references from one contribution to another would have been useful, and would have given a greater appearance of unity to the book. One cannot but feel that Professor Carpenter might well have been asked to contribute a more directly biological article, instead of a description of an instrument for general analysis which is applicable to certain biological investigations. Moreover, an article given over to a very detailed account of one elaborate instrument, however excellent, is of doubtful value to anyone who is not going to the length of buying an apparatus of exactly that pattern.

In a work of this scale, which in no way aims at brevity, it is allowable, if anywhere, to give space to any tables of factors which may assist calculations. When, however, one sees fifteen and a half pages of tables of corrections of gas volumes to N.T.P. (pp. 567–582), one is inclined to wonder how many people will find this worth while, and would not feel adequately served by a slide rule or by some calculator such as Farmer's nomograph (see ANALYST, 1910, **35**, 396).

The print and paper are excellent, and the diagrams clear.

H. R. AMBLER

PHYSIKALISCHE METHODEN DER ANALYTISCHEN CHEMIE. Vol. I. SPEKTROSKOPISCHE UND RADIOMETRISCHE ANALYSE. By G. SCHEIBE, H. MARK and R. EHRENBERG. Pp. x+388. Leipzig: Akademische Verlag. 1933.

This volume is the first of two volumes on physico-chemical methods of analysis which are being compiled under the editorship of Dr. Böttger of Leipzig University. The present volume consists of three sections by eminent contributors. The first on Spectrum Analysis is by Dr. Scheibe, 175 pages; the second, on X-ray Spectrum Analysis, is by Dr. Mark, 148 pages; and the last, by Dr. Ehrenberg, deals with Radiometric Analysis. The treatment of the three subjects is essentially that of a laboratory manual, for especial attention is directed to the various types of apparatus and the technique of the different methods. Moreover, the first two sections contain excellent tables giving the intensities and wave-lengths of emission and X-ray spectral lines, respectively. In the last section, which is based on the work of Hevesy and Paneth and of Ehrenberg, ingenious methods are described of carrying out analytical determinations of widely differing types by the use of various radio-active indicators. Although such an indicator, "Radiothor," is now procurable *in gut emanierenden Zustand* at about 100 RM. per 1 Radium-Milligram-Equivalent, the method is very expensive, and is likely to find only limited application. The book, which is replete with references to the original memoirs, is well-written and produced, and, being authoritative, should appeal to all who are interested in these subjects.

H. T. S. BRITTON

"ANALAR" STANDARDS FOR LABORATORY CHEMICALS. The British Drug Houses, Ltd., and Hopkin and Williams, Ltd. Pp. xvi+296. Price 3s. 6d.

The preparation of fine chemicals in this country has, since 1914, progressed to such an extent that English laboratory chemicals are of as high a standard as those produced in any other country. This progress is reflected in the book recently published conjointly by the two firms who have done much important work in the production of fine chemicals for laboratory use. Each firm has, in the past, published its own book of specifications for analytical reagents, and both have been very useful; the new publication, in which the knowledge and resources of both companies have been pooled, should make an even stronger appeal to chemists than the previous ones. There are in it over 200 specifications, for practically all the reagents that a chemical laboratory is likely to need, and these are not merely statements of the amounts of the various impurities likely to be found in each, but contain short descriptions of the tests used in determining such impurities. The explanatory notes and appendices contain valuable information that should prove very useful to all laboratory workers. No analyst can afford to be without this volume, which will also be of great assistance to industrial laboratories.

S. G. STEVENSON

ANCIENT EGYPTIAN MATERIALS AND INDUSTRIES. Second Edition, Revised. By A. LUCAS, O.B.E., F.I.C. Pp. 447. London: Edward Arnold & Co. 1934. Price 16s.

It is a matter for congratulation that since the publication of the first edition in 1926 (ANALYST, 1927, **52**, 59) the author should have so progressed in his researches as to be able to present, in this new edition, a work altogether more complete and mature. Much of the subject-matter has been re-arranged and amplified; several fresh chapters have been added (necessitating an amplification of the title to include "Industries"), these dealing, *inter alia*, with brewing, faience-making, glass-making, metal-working, mining, pottery-making, quarrying, stone-working and wine-making. The knowledge of materials has been greatly increased by tracking down cross-references in scientific, classical and archaeological literature, and not least by practical studies carried out in the laboratory.

Mr. Lucas, with his long experience in the chemical world and his well-known sympathetic leaning towards Egyptian archaeology, is eminently qualified to produce a text-book of this kind, for a text-book it is, of almost encyclopedic proportions, and one which is destined to become a classic.

The task of compiling such a work has been complicated by the difficulties attending the translation of the names of chemical substances in the ancient records, and, further, by the unscientific descriptions of their finds by many of the early excavators. There is in future little excuse for errors of the second class, for the book abounds with definitions and a healthy scientific dogmatism regarding nomenclature. It forms a striking contribution to Egyptian archaeology.

If it is so received by the archaeologist, the appeal to the scientist cannot fail to be almost equally strong, because for him it is that rare phenomenon, a book which is extraordinarily easy to read and digest, while being at the same time an authoritative reference work dealing with a subject which is not devoid of a certain glamour and of intrinsic scientific interest. The whole is knit together by a short Chronological Introduction and a concluding chapter devoted to a Historical Summary. The technician will appreciate accounts of the early efforts of a primitive people to make pottery, glaze and alloys and to work in wood and metal; the analyst cannot fail to be entertained by some of the more out-of-the-way problems of identification and by the light which is thrown upon the changes undergone by common substances in process of time. A lengthy appendix is devoted entirely to a collection of analytical data.

Of the new matter presented, the first chaper on "Alcoholic Beverages and Sugar" is of outstanding merit. When one considers the slender material available for analysis, and how even this has become transformed with time, it is surely a feat of scholarship to have presented a picture of the industries concerned which is so complete and convincing. Unfortunately, the same cannot be said of the section on "Faience and Glass." Here we find statements which, in being too emphatic, are almost bound to mislead. For example, from statements on p. 106, the implication seems to be that pottery was not glazed in Egypt prior to the Arab conquest (A.D. 640), when lead and salt glazes appear. This is surely not so certain. Glazed pottery, be it remembered, is known in Mesopotamia from as early as the second millennium B.C. Glazed pottery of Persian origin has also been found in Egypt dating from the sixth and fifth centuries, B.C., and from later periods. Examination of some of these specimens suggests that the ancients must have had a way of using their glaze direct on baked clay, so that its contraction on cooling did not tear the surface of the ware. The statement that "vitreous glazes . . . are only satisfactory on highly siliceous material" is essentially correct (with the exception of the glazed steatite group later referred to), but it would seem to leave no room for the vagaries of technique and the variations in the materials which have resulted in the many good examples of ancient glazed pottery that have come down to us.

The book is well printed and, considering the number of footnotes, remarkably free from error. A group of references has been omitted from p. 91, and other minor flaws in the text occur on pp. 135 and 305. One regrets that a work of such obvious merit is not accompanied by maps and by a selection of line blocks from the tomb paintings, illustrating the ancient craftsman at work (good examples of which are on the paper wrapper), but perhaps the author is reserving this for a later re-incarnation. H. J. PLENDERLEITH

THE BUCHEUM. By Sir ROBERT MOND AND OTHERS. Large 4to. 3 Vols. Egypt Exploration Society, Manchester Square, London. 1934. Price 50s.

These three volumes deal with the excavations carried out from 1927 to 1932 in the burial places of the sacred bulls and cows of Ancient Egypt—the Bucheum and the Baqaria—sites in use from the fourth century B.C. until the end of the third century A.D. The supposed miraculous birth, the ceremonies of installation (attended by the king in person), the processional splendour of the triumphal progresses through the country, the elaborate ritual associated with the mummification and funeral rites after death, and the transport of the sacred bull to the huge sarcophagus in the Bucheum, together form one of the most amazing chapters in the history of animal worship.

The detailed summaries of the discoveries and the discussions of their significance show the extent to which the modern archaeologist relies on the expert to assist him in the study and interpretation of the data collected. The list of contributors includes the names of experts in metallurgy, mineralogy, petrology, textiles, wood, osteology, and ancient musical instruments. In this work the analytical and the metallurgical chemists have played an important part. A few of the more interesting methods and results may be mentioned here.

For cleaning copper and bronze objects, cold 25 per cent. sulphuric acid has proved most useful. Great care must be taken to remove all traces of acid after treatment, and washings are repeated until no reaction is given with B.D.H. Universal Detector, which will show the presence of as little as 1 part in 8 millions. A solution of Rochelle salt and sodium hydroxide proved effective in removing obdurate corrosion. After this treatment, the scratches due to ancient sand-cleaning were clearly visible.

Details are given of analyses which throw much light on the use and composition of alloys and on methods of manufacture. It seems clear that the ancient craftsmen knew that the addition of lead to the copper-tin alloys facilitated casting and subsequent engraving. On wire, the ancient draw-marks are visible, pointing to the method of manufacture by drawing through a rather rough die. Microscopic examination has shown that the metal had been cold worked and annealed many times from the original cast ingot. The lead-content is low (less than 1 per cent.), showing that the Egyptian was aware of the harmful effect of lead in alloys subjected to considerable cold working. The harder-wearing properties associated with a higher tin-content also appear to have been recognised, for the tin-content is kept low in cases where a large amount of hammering was necessary to reduce the thickness during manufacture. Clamps (88 per cent. Cu) used for the attachments of bandages to secure the limbs of the mummified bull, appear to have been drawn in square section or hammered from round wire.

An enema (used in the purification of the intestines—the bull was not eviscerated) consists of a vessel of very leady bronze, furnished with a spout, which was affixed by running molten bronze over the two portions held in a mould. The excess of metal was smoothed off, after cooling. Minute blow-holes in castings were troublesome, as they are occasionally now. They were often made good by casting on metal of similar composition and smoothing off. A more ancient method was to insert a solid plug of bronze and hammer over the ends.

A flute, with four finger holes, had been made by thinning down from a slab casting. The material was then cut to size and bent to shape, and the joint soldered. The analysis of the solder agrees with that of best-quality solder in present-day use.

A mixture of resin and whiting was used as an adhesive for fastening stone and glass inlay in jewellery and other objects. White of egg was employed for cementing gold leaf on plaster.

It is suggested that analyses on a large scale of coins from various mints, and of ores from different mines, might enable the metallurgist to determine at what point the percentages of tin, zinc, iron, etc., may be regarded as intentional, and also, if they prove to be impurities, to decide whence the ore was obtained.

These volumes, like all the publications of the Egyptian Exploration Society, are a model of what the records of excavation should be. The plates, of which Volume III is entirely composed, are excellent. R. W. SLOLEY

DUST. By S. C. BLACKTIN, M.Sc., Ph.D., A.I.C. Pp. xii+296, with four illustrations. London: Chapman & Hall, Ltd. **1934.** Price 18s. net.

This volume comprises a co-ordinated summary of the widely-scattered European and American literature on dusts, and appears to be the first of its kind to deal with this very extensive subject. That such a compilation was needed is indicated by reference to two well-known and comprehensive scientific dictionaries, in neither of which is a general article on dust to be found. The contents of this work include the production of dusts and smokes in nature, everyday life and industry, their distribution and characteristics, physical, physiological and pathological effects, enumeration, elimination, and methods employed in their scientific investigation. It is evident that the author has shown extreme assiduity in the production of his book, for the list of references contains considerably over 500 items, ranging from Homer's "Iliad" to articles in *Nature*, dated June, 1933. The text, however, is far more than a collection of extracts from the works mentioned, for it is a more or less continuous narrative including erudite criticisms and interpositions by the author, with in some degree the overlapping inevitable in a work of this description.

Dr. Blacktin has coined the name "Staubosphere" for the dust-content of the atmosphere, although the term would have been more appropriate to an atmosphere charged with dust. From the text it is evident that he is an enthusiast on his subject, even tending to convey to the reader's mind an idea that the one thing of importance in human life in its many phases is dust. This is by no means unnatural, and allowance will readily be made for it, but at times the author's concentration has resulted in a disrespect for correct grammar, spelling, and the lucid and simple style so essential in a scientific text-book, while the continuity of the narrative is occasionally broken by excessive punctuation and by the introduction of abrupt (and in one case) verbless sentences.

From the text we learn that it is only within recent years that attention has been directed to the investigation and amelioration of the effects of dust, although Georg Agricola in the sixteenth century recognised the poisonous nature of metal dusts, and in 1721 pathological effects were attributed to the inhalation of stone dust. Incidentally, the contributions to our knowledge of bacteriology made by a pure physicist, John Tyndall, about the year 1870, are recalled.

Perhaps the weakest section of the whole book is that consisting of 16 lines only, and dealing with "Dust and Crime." The names of two popular writers are given, but no mention is made of Gross, Locard, Lucas, and others, or of the paragraphs on dust published occasionally in THE ANALYST. It is, perhaps, invidious to mention that in a volume of this nature one naturally expects to find some reference to the physical, chemical and microscopical identification of dust particles—a subject of increasing importance in scientific investigations—but this has been omitted.

But few errors of fact occur in the text, although on page 232 a redundant acute accent is placed over the final letter in E. H. Kettle; the term "Brewing" is substituted for "Malting" on p. 235, and on p. 202 the fumes of burning sulphur used for fumigating glass-houses are stated to combine, forming *zinc sulphate*. This may possibly refer to the action of the gaseous products upon zinc vessels in the houses, but, if so, this should be stated.

The last 40 pages of the book contain a glossary giving the metric and English linear and cubic equivalents, an extensive table of references mentioned above, and both author- and subject-indexes. These all show a high degree of accuracy, but the subject-index requires extension.

Notwithstanding its faults, this work forms an exhaustive and valuable compilation which will not only serve to show what has been accomplished in the past, but will also indicate to future workers the immense field still open for further investigation. Though future editions should be subjected to more drastic proof-reading before publication, the author is to be congratulated upon the zeal with which he has collected material from a vast number of sources—a task which must have proved onerous indeed.

T. J. WARD

LUMINESZENZ-ANALYSE IM FILTRIERTEN ULTRAVIOLETTEN LICHT. By P. W. DANCKWORTT. Third Edition. Pp. 190. Leipzig: Akademische Verlagsges. m.b.H. Price RM. 8.50.

The name of Professor Danckwortt will be familiar to all readers of THE ANALYST, for his descriptive summary of the analytical applications of ultra-violet rays, which was one of the earliest collective contributions on the subject, appeared in this journal (1927, **52**, 707). Since then the first edition of this book was published (1928), and the author is to be congratulated upon it being so successful that two more editions have been required within the short space of six years. The present volume, which contains 47 pages more than the last edition, follows the arrangement of its predecessors: it begins with a description of the different types of lamps and accessory apparatus, including an outline of the practical technique, and then systematically summarises recorded results under their appropriate headings (pharmacy, botany, technology, etc.). All these sections have been brought up to date, and the references cover a very wide range of journals. In this connection it is of interest to note that Kitching's pioneering work published in this journal (ANALYST, 1922, **47**, 206) has not been overlooked in the bibliography, which contains 890 entries, as compared with 315 in the second edition.

The new matter in Chapter XIII, which deals with photographic methods of recording ultra-violet phenomena, will be found particularly useful, for it gives full practical details of the technique, including that of photomicrography, and is well illustrated by typical examples.

The last chapter (XVI) occupies 33 pages, and is essentially a complete treatise, written by Dr. J. Eisenbrand, on quantitative measurements relating to fluorescence. It deals, *inter alia*, with the distribution of fluorescence intensities over the spectrum, physiological aspects of fluorescence colours, "fluorometry" and fluorescence indicators, the measurement of light absorption with the aid of fluorescence indicators, and the theory of fluorescence phenomena. The whole chapter is a welcome contribution towards the systematisation and elucidation of the physical laws that underly the plethora of isolated empirical results recorded in the literature. This section, alone, makes the book worth acquiring, even by those who possess the previous editions.

EDITOR

FEBRUARY, 1935 Vol. 60, No. 707

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS
AND OTHER ANALYTICAL CHEMISTS

The Identification of Common Edible Sea Fish
(with Demonstration)*

By C. HATTERSLEY (Chief Inspector, Fishmongers' Company)

(Demonstrated at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry, November 14, 1934)

THE distinctive characteristics of twenty-two species of common edible sea fish were demonstrated on actual specimens. The following are among the most important features to be studied:

COD.—The body of the cod is thick and rounded near the head, but tapers off suddenly towards the tail. The fish is of a greenish or brownish-olive colour with numerous yellowish or brown spots. It has a white lateral line, the upper jaw is large, and there is a barbel on the chin. There are 3 dorsal, 2 pectoral, 2 ventral (jugular), and 2 anal fins.

HADDOCK.—This is similar to the cod, but is smaller and may be distinguished by a black lateral line and a large blackish spot above the pectoral fin—the so-called finger-and-thumb marks. It has a small barbel on the chin. The colour is darker than that of cod, and, when first caught, the fish is of a beautiful bronze colour. It has 3 dorsal, 2 ventral, 2 pectoral, and 2 anal fins. The scales are rather large.

WHITING.—This is smaller than the haddock; the head and body are compressed; the deepest part is at the vent, which is opposite the middle of the first dorsal fin; eyes moderately large; there is no barbel on chin; the scales are small and silvery; the skin is of a dusky yellow colour, the sides paler and the belly silver-white; there is a black spot on the upper side of the root of the pectoral fin. There are 3 dorsal, 2 pectoral, 2 ventral, and 2 anal fins.

HAKE.—This is another elongated fish. It has no barbel but, unlike the ling, has large scales and a large mouth with exceedingly sharp teeth. The colour is dark grey on the back and slightly lighter on the belly. It has 2 dorsal, 2 pectoral, 2 ventral, and 1 anal fin.

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* The Ministry of Agriculture and Fisheries has drawn up a list (Fisheries Notice No. 23) of the names under which it is recommended that sea fish should be sold to the public. Reference to this will be made in the March issue of THE ANALYST.—EDITOR.

COALFISH.—This is similar in size to the cod, of a dark slate-blue colour, almost black on the back and sides, graduating to grey on the belly; the scales are large. It has no barbel. The lower jaw is slightly longer than the upper. A white lateral line is shown, and there are 3 dorsal, 2 ventral, 2 pectoral, and 2 anal fins. The usual length is 2 to 3 feet.

POLLACK.—This is similar to coalfish, and is of a dull green colour; belly greyish-white.

LING.—This is an elongated fish with very minute scales and two dorsal fins, the edges of which are tinged with grey; the first is high and short, the second very long, extending almost to the tail. It has a long barbel on the chin. The colour is usually grey on back with white belly.

CATFISH.—The head is removed and the fish skinned, and it is then largely sold as "rock salmon," especially by fish fryers. If exposed in its natural state with the head on, and labelled "Catfish," it would be unsaleable. When skinned it is pink.

DOGFISH.—This is sold and used in frying shops as "flake." It is so called because flakes are distinctly marked all down the body. It is a member of the shark family.

BRILL AND TURBOT.—These are very much alike. The turbot is round and has tubercles on the back, which are absent from the brill.

PLAICE AND DABS.—Plaice can always be identified by the spots on the back. Dabs, which are sometimes sold as plaice, have very much the same shape, but have no spots. The dab is very rough, whilst the plaice is smooth.

LEMON SOLE.—This is very like the dab. If in doubt, one should turn the fish dark side up and look at the lateral line. The line on the dab takes a sharp turn; also, the skin is rough, whereas that of lemon sole is smooth.

SOLE OR DOVER SOLE.—The skin is very dark on the back, very rough, and has a small black speck just at the top of the ventral fin. A useful fact in connection with sole is that, as a rule, it is cooked with its head on, and can then be identified by its curved mouth; hence, if served as "grilled sole" with only half a head, it may be looked upon as suspicious; it may possibly be a witch.

WITCH.—This is often substituted for sole or lemon sole. Lemon soles are whiter than witch. Witch is rather coarse on the front; rather grey instead of white.

MEAGRIM.—This and witch are the only two flat fish not distinctly white in front; they are rather greyish-white. Witch has a small head, small mouth and straight lateral line. Meagrim has a large head, large mouth and curved lateral line.

HAKE, POLLACK AND HADDOCK.—In distinguishing between these species the shape must be taken into consideration. The cutlets from the hake are circular, whilst those from the haddock are oblong; there are also differences in colour, pollack being not quite white, whilst hake is perfectly white. Pollack has only a faint lateral line on the skin, whilst the lateral line on the haddock is dark.

FISHMONGERS' HALL
LONDON, E.C.4

Discussion

Replying to questions, Mr. **Hattersley** said that *uss* was another name for dogfish. *Roker* or *thornback* was of the skate family, but was very heavily thorned on the back. *Lythe* was a local name for *torsk*. *Pouting* was one of the whiting family, but it had a very long barbel on the chin, which was absent from the whiting; it was also much broader in the body. *Flounder* was similar to plaice; it had the same shape, but was distinguished by having sharp spines on the lateral line, and also round the fins. *Bass* was sold in shops as "Salmon Bass." It looked very much like salmon, but the scales were more prominent, and the dorsal fin had five very sharp spines. In colour it was rather grey, graduating to silver. The term "*blue halibut*" had reference to the colour of the upper surface; some were bluish-black, whilst others might be grey-black, according to the grounds where they were caught. *Sardines* and *pilchards* were practically the same fish. When it grew beyond 4½ inches a sardine became a pilchard.

It was possible to distinguish between different fish after they had been skinned and filleted, but it required life-long experience to do so.

The difference between "right-handed" and "left-handed" fish depended upon the position of the eyes when viewed along the fish from the head; thus dab was "right-handed" and meagrim "left-handed." A set of fish scales was kept at Fishmongers' Hall, and when any doubt was raised regarding fish the scales were compared with the standards under the microscope.

Prosecutions had been instituted by the Middlesex County Council against shopkeepers for the substitution of fish. For example, haddock and pollack had been sold as hake, and cod fillets were sometimes sold as "hake" fillets. There was also the possibility that catfish might be filleted and substituted for other fish.

The Composition of Fish Pastes

By H. E. COX, D.Sc., Ph.D., F.I.C.

(*Read at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry, November* 14, 1934)

Although there is recorded in our literature a fair amount of information about meat pastes and potted meat, there is very little on the subject of fish pastes from the point of view of composition. In view of the possible extension of standards and regulations, it seems worth while recording what has been observed as a result of the analysis of a fair number of samples sold in London. Fish pastes have been the subject of regulation with regard to preservatives in most countries, but only in a few in respect of composition or such matters as cereal additions. The addition of farinaceous material, usually bread, is fairly general, though by no means universal, but sometimes the quantity is so large as to amount to dilution or filling. Where limits have been enacted, as in Canada and Switzerland, 5 per cent. of dry starch is general, and in other countries, such as the U.S.A., Belgium, Italy, Australia and New Zealand, a declaration of addition is required.

Fish pastes are essentially factory products, seldom made at home, so that in approaching the question of what they ought or ought not to contain, one cannot start from old-fashioned recipes, and regard must be had to factory conditions of supply, price, transport and processing. Dietetically they are more of a relish than a staple article of diet intended to serve as a meat ration, as a sausage may be. It is difficult, or often impossible, to determine their real composition by analysis, and the named fish is often merely the one giving the dominant flavour. It will, however, be generally agreed that fish pastes ought to be predominantly fish, and ought not to contain excessive proportions of diluents such as water, bread or salt.

For the purposes of the analyst, fish and fish products are conveniently divided into four groups: (i) Fatty fish; (ii) non-fatty fish; (iii) salted fish; and (iv) crustaceans. The percentages of fat and nitrogen in these groups are fairly characteristic and serve as a basis for the calculation of the proportion of fish in the fish pastes made from them. Unfortunately, there are no known methods for determining the identity of fish in a cooked paste, though careful microscopic examination, together with determination of the chemical composition, often affords useful indications. The microscopic appearance of any scales or bits of shell or bristles may help.[1] The following table shows the average composition of the commoner types of fish, of which salmon is much the most important from the present aspect. The data are collected from various sources—Plimmer, König, Atwater and Bryant—together with analyses of my own; all the figures refer to the edible parts of the fish.

TABLE I

	Water Per cent.	Fat Per Cent.	Protein Per Cent.	Ash Per Cent.	Salt Per Cent.	Nitrogen on fat-free basis Per Cent.
FATTY FISH						
Herring ..	72·5	7·1	19·5	1·5	0·3	3·4
Mackerel ..	73·4	7·1	18·7	1·2	—	3·2
Salmon* ..	66·6	10·5	21·5	2·0	0·6	3·9
Sprat ..	66·8	14·5	17·1	1·8	—	3·2
Sardine ..	58·5	8·0	20·5	9·5	—	3·6
NON-FATTY FISH						
Cod	82·6	0·4	16·5	1·2	0·2	2·6
Haddock ..	81·7	0·3	17·2	1·2	0·2	2·7
Hake	83·1	0·7	15·4	1·0	—	2·5
Whiting ..	80·4	0·2	17·7	1·1	—	2·8
SALTED FISH						
Anchovy ..	62·5	8·3	20·9	—	[7 to 20]	3·6
Bloater ..	64·0	14·0	19·0	2·0	0·9	3·6
Kipper ..	61·0	8·5	20·5	6·0	4·9	3·6
CRUSTACEANS						
Crab	73·6	0·2	22·4	2·7	0·3	3·6
Prawn ..	71·2	1·3	22·8	5·2	0·3	3·6
Lobster ..	71·5	1·0	20·7	3·4	—	3·3
Shrimp ..	70·0	0·9	22·0	6·8	1·5	3·6

* As canned.

Pacific salmon are said to be richer in fat than Atlantic salmon.

In all cases protein means nitrogen multiplied by the conventional factor, 6·25. Usually the analysis of fish in these terms adds up to something rather less than 100 per cent., and the presence of small quantities of glycogen or other carbohydrate has been reported in many cases. Starch is never found as a natural constituent, so that, apart from any minute quantity due to condiments, its presence in fish paste always indicates bread or other filler. The amount of salt in anchovies, kippers and bloaters is apt to vary widely, and sometimes anchovy or bloater paste will contain quite large additions of salt. The following tables set out the analytical results obtained with a number of fish pastes; where I have analysed an adequate number of different brands the maximum, minimum and average are shown, but with other varieties, for which only one typical result is given, the figures are less representative.

TABLE II

	Salmon and shrimp 16 Samples			Bloater 9 Samples		
	Max. Per Cent.	Min. Per Cent.	Average Per Cent.	Max. Per Cent.	Min. Per Cent.	Average Per Cent.
Water ..	68·04	57·58	63·8	59·26	45·00	55·6
Fat ..	11·73	7·56	9·3	16·86	7·80	12·0
Protein ..	20·21	16·46	18·2	23·06	19·31	20·1
Ash ..	6·22	2·96	4·0	9·31	4·29	6·7
Salt ..	4·50	1·60	2·0	7·15	2·50	4·8
Starch ..	8·68	None	4·2	12·30	None	4·0

TABLE III

	Anchovy 9 Samples			Sardine and tomato	Salmon and anchovy
	Max. Per Cent.	Min. Per Cent.	Average Per Cent.	Per Cent.	Per Cent.
Water	65·60	38·12	55·7	60·39	63·02
Fat	38·13	0·90	12·1	9·60	9·12
Protein ..	22·98	17·60	20·6	18·95	14·04
Ash	16·70	4·01	7·1	3·35	5·32
Salt	14·20	3·32	5·9	Sugar 7·73	—
Starch ..	12·7	Absent	2·5	None	8·50

TABLE IV

	Lobster Per Cent.	Crab Per Cent.	Prawn Per Cent.	Shrimp Per Cent.
Water	68·77	66·70	66·20	64·72
Fat	9·83	5·19	8·56	11·50
Protein	15·53	18·79	21·60	18·37
Ash	3·10	2·56	3·98	2·99
Salt	1·02	0·60	1·70	1·82
Starch	3·05	6·76	None	2·50

Besides the main ingredients shown, small additions of pigments, such as bole, or of artificial dyestuffs, are fairly common. In my observation, fish pastes which contain large proportions of starchy matter and water do not keep so well when the pots are opened, but are rather susceptible to mould growth. Preservatives are, of course, prohibited in this country, and so are not found, except that an occasional trace of boric acid may be detected if shrimps or other fish have been dusted therewith, and faint traces of formaldehyde may arise from natural causes.[2] One other abnormality in fish pastes is the presence of minute crystals of magnesium ammonium phosphate in the form of struvite, which is liable to be mistaken by the customer for glass. I have found these quite often in canned crayfish, shrimps and lobster. Manley[3] records their presence in tinned salmon. They may be as much as 5 mm. in length.

The calculation of the approximate composition of the paste is not difficult when the identity of the fish used is known; without such knowledge one can only proceed on the basis of probability fortified by the name on the label. The method is an extension of the lines adopted by Stubbs and More[4] for the determination of the proportion of meat in sausages.

The starch percentage, multiplied by 1·7, gives moist bread containing 40 per cent. of water and 1 per cent. of nitrogen. The nitrogen found, less 1 per cent. of the bread, multiplied by 100 and divided by the nitrogen per cent. in the fat-free fish used, gives the fat-free fish, to which must be added the fat found if its amount be not in excess of that natural to the percentage of fish indicated. When there is much fat, it is desirable to examine it in detail to ascertain its nature and origin. If there is no indication of the addition of butter or other foreign fat, any excess usually indicates the use of a fatty-fish basis such as salmon, which is common in crab, lobster and shrimp pastes. The proportions of salt and water natural to the fish are calculated from the fish basis, and any excess is noted.

As salmon is the commonest basis in mixed pastes, it is convenient and approximately correct to take its composition as the starting-point in attempting to calculate the ingredients of a mixture. The proportion of fat present helps in this direction; for example, in the shrimp paste shown there is much more fat than is found in shrimps, and it agrees approximately with that in a salmon basis. In another case, anchovy paste contained only 0·9 per cent. of fat, so that not only could there be but little anchovy in it, but the basis must have been a non-fatty fish of which the nitrogen basis is about 2·6 or 2·7. Two instances will show what sort of result may be expected. The crab paste shown in Table IV contains 5·2 per cent. of fat, so that it evidently contained a basis of nearly 50 per cent. of fatty fish—salmon; hence the nitrogen basis may be taken at, say 3·7, instead of 3·6 for shrimp or 3·9 for salmon. The starch percentage (6·76) is equivalent to 11·5 per cent. of bread, and so accounts for 0·11 per cent. of nitrogen and 4·5 per cent. of water. The nitrogen, less 0·11, is 2·90 per cent., which corresponds with 78·4 per cent. of fat-free fish or 84 per cent. of total fish, including 67 per cent. of water. Thus the composition works out at:

Fish	84 per cent.
Bread	11 ,,
Added water	5 ,,
	100 ,,

Similarly, the composition of a salmon and shrimp paste giving the analytical data shown in the average in Table II can be calculated on a nitrogen basis 3·8, and corresponds to:

Fish	85 per cent.
Bread	7 „
Added water	5 „
Added salt	1 „
	98 „

These methods of calculation are put forward only tentatively, with the realisation that they are imperfect, and would be vitiated by a variety of circumstances. It is hoped that before long someone will discover a method which will enable us to identify and estimate any particular kind of cooked flesh.

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DISCUSSION

The CHAIRMAN (Dr. L. H. Lampitt) said that the subject of this paper was obviously one of intense interest, and one on which there was only very meagre information available. As Dr. Cox had already pointed out, certain pastes contained more than the amount of fat consistent with the type of fish used, but the possibility that it was essential to add fat, in order to obtain the desired palatability and consistence, must always be considered in connection with a product which was sold virtually as a luxury and not for its food value.

Professor J. C. DRUMMOND suggested that the new technique for examining by adsorption would probably enable one to identify the pigments of the fish used in the paste. Much work had been done on the subject by German chemists, and he thought that in some cases the process would be very simple. It might, for instance, be possible to distinguish in this way between the pigments from the salmon and the anchovy. Quite small amounts of hydrocarbon and related carotinoid pigments could now be separated from oils by this method, and it might be possible by this means to differentiate certain fish.

Mr. C. E. SAGE remarked that the difference in price between various fish pastes depended largely upon the market value of canned goods. *Real* shrimp extract was sold at 15s. per lb. The difference in price between fresh and canned Alaska salmon enabled the manufacturers of salmon paste to make an immense profit. When it was a question of cheapness one had to keep a careful watch on these products, and frequently the analyst was the only safeguard between the manufacturer and the consumer. The results put before them by Dr. Cox would enable them to form an opinion regarding some of the products upon which analysts had to report.

Mr. MORGAN asked what would be the effect on the calculation of the composition if soya flour were used as a filler instead of ordinary bread.

Mr. J. W. BLACK asked whether Dr. Cox had been able to compare actual formulae with calculated formulae?

Mr. JOHN EVANS asked why the filler had been calculated as bread. Surely, manufacturers would be much more likely to use rusks.

Mr. STEVENSON asked if Dr. Cox had determined the copper-contents, especially in pastes made from crustaceans, the blood of which contained large amounts of copper and which were usually killed by boiling, so that no blood was lost.

Mr. T. MACARA asked if the figures used in the calculations had been compared with those of a number of the natural products. He was quite sure that there must be a wide variation in the composition of fish, and just as variation in pork affected the calculation of the composition of sausages, so variation in the fish must affect the calculations in the case of paste. He agreed with Dr. Lampitt that the manufacturer must add material to make the article spread well, to have a nice flavour and generally to be appetising, and he thought that these things should be kept in mind when dealing with a manufactured product. With regard to remarks made about fish paste being a profitable line—a good deal too much was made of this—the price indicated the product and an article would practically always find its true level of price in the market.

Dr. Cox, replying, said that he had no experience of the method mentioned by Professor Drummond, but would be very glad to have details of it. He had not come across the *real* shrimp paste to which Mr. Sage referred. With regard to the different fillers which had been mentioned by Mr. Evans and Mr. Morgan, he thought that bread was the most usual, but it would be quite simple and appropriate to calculate the results in terms of rusks or like material, if one so desired. Soya flour in any substantial quantity would disturb the protein in relation to the other constituents, and he thought would be detectable. He agreed with Mr. Macara about the wide variations possible in the composition of fish, but surely one could only take averages as a basis of calculation. It would be much better to base calculations on fat and protein percentages rather than on traces of impurities, such as copper, which might be picked up from pans or other utensils.

Notes on Fish Pastes

BY C. H. MANLEY, M.A., F.I.C.

(Read at the Joint Meeting of the Society with the Food Group of the Society of Chemical Industry)

FOLLOWING the suggested standard put forward by Manley and Sutton[1] for potted meat, in which a maximum water-content of 70 per cent., together with the exclusion of starch, were advocated, it was felt that similarly, in a product sold as potted salmon, starchy filler should also be excluded.

Accordingly an attempt was made in the Leeds police court on May 5th, 1931, to emphasise the distinction between "potted salmon" and "salmon paste."[2]

A sample of food sold by a shopkeeper as "potted salmon" was found on analysis to contain 80 per cent. of salmon and 20 per cent. of a starchy filler, the proportion of the latter being calculated from a 6·6 per cent. anhydrous starch-content, 33 per cent. being taken as an average total solid figure for the starchy filler used. (Owing to the swelling of the grains during cooking it was not possible to identify the particular starch present.) The percentage of salmon, *viz.* 80 per cent., calculated from the protein-content, supported the figure obtained for the starchy filler.

That a distinction should be drawn between the two products was admitted by the Stipendiary Magistrate, who dismissed the summons under the Probation of Offenders Act on payment of costs, defendant not having made the sample and having charged only the commercial rate for salmon paste, and not that for potted or tinned salmon.

Whilst one might reasonably expect to find a certain proportion of starchy filler in products sold as fish paste, it is significant that one well-known manufacturing firm last year published on a full-page advertisement in a London newspaper an analysis of its salmon and shrimp paste, from which starch apparently was excluded, the fish-content being given as 97 per cent., and the remaining 3 per cent. as butter and seasoning.

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The Detection and Determination of Triethanolamine

BY H. RONALD FLECK, A.I.C.

THERE does not appear to be any published method for the determination of triethanolamine in toilet creams and emulsions. Compounds suitable for identification have been described by Jaffé[1], who prepared the complexes $(CH_2OH.CH_2)_3NH.BiI_4$, m.p. 193° C., and $(CH_2OH.CH_2)_3NH.SbI_4$, m.p. 174° C. The reaction of triethanolamine with cobalt salts in ammoniacal solution has been used as a test for the base by Garelli and Tettamanzi.[2]

In the routine analysis of creams in which a fatty basis is incorporated with water, the material is saponified and evaporated to dryness with lime, and the powdered residue is extracted with boiling absolute alcohol. The alcoholic extract, on evaporation, yields a viscous residue containing any triethanolamine, glycerol, or ethylene glycol which may have been present in the original material.

In the course of the present work it was found that commercial triethanolamine gave with hydriodic acid of constant boiling-point, a white crystalline substance which agreed with the composition $(CH_2OH.CH_2)_3N.HI$, and contained 53·6 per cent. of the base. This compound, on crystallisation from absolute alcohol, melted sharply at 169° C., the m.p. being unaltered by further recrystallisation. The hydriodide is somewhat soluble in ethyl alcohol, but practically insoluble in *iso*-propyl alcohol. The small solubility in this solvent has been determined and found to be 1 mg. per ml. at room temperature.

The following method based on these observations has been worked out:

METHOD.—An accurately weighed portion (about 0·5 g.) of the viscous residue from the alcoholic extraction described above is evaporated to dryness with 0·5 ml. of constant-boiling 57 per cent. hydriodic acid and 5 ml. of water in a glass dish. The residue is stirred with 5 ml. of pure *iso*-propyl alcohol, transferred to a 1.G.3 sintered glass crucible, and washed three times with 5-ml. portions of the alcohol, the crystals being sucked as dry as possible after each washing. The crucible and contents are dried to constant weight at 100° C., and a correction of 1 mg. for each ml. of *iso*-propyl alcohol used in the transference and washing of the crystals is applied. The m.p. of the product (169° C.) serves to identify triethanolamine. The weight obtained, multiplied by 0·536, gives the weight of triethanolamine present.

The method was tried on commercial triethanolamine, and also on triethanolamine purified as follows:

To about 20 g. of the base, dissolved in 50 ml. of 95 per cent. ethyl alcohol, were added 40 g. of 57 per cent. hydriodic acid. The resulting crystals were collected and recrystallised three times from 95 per cent. ethyl alcohol. A weighed quantity was dissolved in water and the exact amount of freshly precipitated silver oxide required to combine with the hydriodic acid in the compound was added. The mixture was well shaken for some time and filtered from the silver iodide. The filtrate was evaporated to dryness with a small amount of lime, extracted with absolute alcohol, and dried to constant weight at 50° C. *in vacuo*.

Results of typical experiments on this purified material were:

Pure triethanolamine taken	HI used	Weight of hydriodide	Triethanolamine found
g.	ml.	g.	g.
0·2663	0·5	0·4963	0·2660
0·5228	1·0	0·9746	0·5224

COMMERCIAL TRIETHANOLAMINE.—Commercial triethanolamine usually contains small amounts of the mono- and di-ethanolamines, together with some water. To study the effect of the mono- and di-substituted amines on the precipitation of the hydriodide a commercial sample was carefully fractionated *in vacuo*, in order to obtain the lower-boiling fractions. These were refractionated to give nearly pure mono- and di-ethanolamines, having the following constants:

	Approx. mol. weight	$n_D^{20°}$
Monoethanolamine ..	65·7	1·4445
Diethanolamine ..	99·4	1·4702

When each of these substances was tested by the method the material was entirely soluble in *iso*-propyl alcohol and no crystals were obtained. A mixture of these two products with the purified triethanolamine described above, gave the following result:

Mono-	di-	tri-	Weight of hydriodide obtained	Weight of triethanolamine found
	ethanolamine			
			g.	g.
0·0624	0·1150	0·3020	0·5626	0·3015

From this it is clear that the presence of mono- and di-ethanolamine does not interfere with the determination.

Commercial triethanolamine (4·3554 g.) was dissolved in water, and the solution was diluted to 100 ml.; 10 ml. were used for each analysis, the following weights of hydriodide being obtained:—(*a*) 0·7124 g., (*b*) 0·7258 g., (*c*) 0·7320 g., (*d*) 0·7100 g. Mean of 4 determinations: 0·7200 g. of hydriodide. The sample therefore contained 88·6 per cent. of triethanolamine.

The method gives moderately satisfactory results when glycerol or ethylene glycol is present, as the following figures show:

DETERMINATION IN THE PRESENCE OF GLYCEROL.—Varying weights of the purified base were mixed with known weights of glycerol, and the mixtures were dissolved in water and analysed. The results were as follows:

Weight of triethanolamine taken g.	Weight of glycerol taken g.	Base Per Cent.	Weight of triethanolamine found g.	Error Per Cent.
0·7597	0·2462	75·3	0·7527	−0·9
0·3859	0·4560	45·8	0·3903	+1·1
0·3859	0·9120	29·7	0·3751	−2·7
0·3859	1·3680	21·8	0·3696	−4·2
0·2348	2·5276	8·5	0·2266	−3·5

DETERMINATION IN THE PRESENCE OF ETHYLENE GLYCOL.—Varying weights of the pure base were mixed with known weights of pure ethylene glycol, and the mixtures were dissolved in water and analysed. The results were as follows:

Weight of triethanolamine taken g.	Weight of glycol taken g.	Base Per Cent.	Weight of triethanolamine found g.	Error Per Cent.
0·8043	0·2362	77·3	0·8011	−0·4
0·6208	0·3886	61·5	0·6170	−0·6
0·4335	0·6336	40·6	0·4210	−2·8
0·2640	0·7454	26·15	0·2587	−2·0
0·1970	1·8635	9·56	0·1903	−3·4

The method has also given satisfactory results with solutions of triethanolamine stearate and oleate, since these are decomposed by the hydriodic acid, with the production of triethanolamine hydriodide and the corresponding fatty acid, which is soluble in the *iso*-propyl alcohol.

I wish to thank Dr. A. M. Ward for his interest and helpful criticism during the course of this work.

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A new Method for the Colorimetric Determination of small Quantities of Iodide in presence of other Halides

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IN a previous communication[1] we have shown that iodine can be determined colorimetrically by treating a solution of an iodide with acid permanganate and extracting the liberated iodine with carbon tetrachloride.

The method has been developed, and we have now succeeded in determining iodide colorimetrically in presence of fluorides, chlorides and bromides by oxidising an iodide solution with nitric acid before extracting the iodine with carbon tetrachloride. Maljaroff and Matskiewitsch[2] determine iodine by using nitrous acid and chloroform, but the iodine-chloroform extract obtained by their method remains turbid and does not become fit for colorimetric comparison for about an hour after the extraction is made, whereas the method described below gives quite a clear extract which can be matched immediately.

It has been found that acid permanganate ($N/50$ potassium permanganate with dilute sulphuric acid), which was successfully used in liberating iodine from a pure solution of an iodide, is not suitable for the determination of iodides when present with bromides. By using nitric acid of suitable strength, however, the iodides are selectively oxidised with liberation of iodine, whilst the other halides are not affected in any way.

The presence of other salts, such as the sulphates, phosphates or nitrates of sodium, potassium, calcium, magnesium, etc., either individually or in mixtures, does not interfere either with the extraction of iodine or with the production of the proper tint of the extract. If the concentration of the halides, especially that of magnesium iodide, does not exceed 1·5 per cent., the extraction and accurate determination of iodine can be carried out quite satisfactorily. No loss of iodine results from the presence of the salts contained in sea-water.

To obtain an accurate result the iodide solutions should be diluted to a concentration of about 0·01 per cent., so that a very small amount of the oxidising agent will liberate iodine without oxidising the bromides. If, on the other hand, a higher concentration of the iodide solution is employed for the determination, it will necessitate the use of a comparatively larger quantity of nitric acid, which is likely to decompose the bromides as well. The bromine so liberated will change the colour of the iodine solution and so render the test useless.

The reagents and apparatus required are as follows:—(1) Pure nitric acid (sp.gr. 1·4) diluted to about 5 N.[3] (2) Carbon tetrachloride (b.p. 76° C.). (3) Standard potassium iodide or sodium iodide solutions of concentrations varying from 0·0005 to 0·01 per cent., as required. (4) Separating funnel, 50 to 100 ml., with a short stem. (5) A colorimeter of the Duboscq type.

PROCEDURE.—(*a*) *Preliminary Estimation.*—With the view of forming an idea of the depth of colour that will be produced by a definite volume of the unknown solution and the minimum amount of nitric acid required for complete oxidation, a preliminary test may be found useful. Five ml. of carbon tetrachloride and

10 ml. of the unknown solution are put into a test tube, and nitric acid is added, drop by drop, from a burette, until the resulting brown colour of the upper layer ceases to increase in intensity. When the test-tube is shaken, the carbon tetrachloride takes up the liberated iodine and becomes pink. The amount of nitric acid used is noted. It has been found that for 10 ml. of a 0·01 per cent. iodide solution about 2·5 to 3 ml. of nitric acid are sufficient to complete the oxidation. If it is seen that the tint thus obtained is too deep or too pale, the amount of the unknown solution taken should be decreased or increased accordingly. Tints either too deep or too pale are not suitable for comparison, because the smaller degrees of difference cannot be accurately judged. The depth of colour in this preliminary colour-test gives an idea of the concentration of the standards to be selected for the actual determination. The choice of the right depth of the tint is a matter of experience which is readily gained by a couple of determinations.

(*b*) *Actual Determination.*—About 5 ml. of carbon tetrachloride are placed in a separating funnel, and a definite volume of the unknown solution, an idea of the iodine-content of which has already been formed in (*a*), is introduced. Then about 2·5 ml. of nitric acid are slowly added from a burette directly into the solution and not down the sides of the vessel. The funnel is at once shaken vigorously, and the liberated iodine is taken up with carbon tetrachloride, leaving the upper layer colourless. The carbon tetrachloride extract is transferred to a graduated test-tube, about 4 ml. of carbon tetrachloride are added to the solution, and about 1 ml. is allowed to flow through the funnel (without shaking) into the test-tube to rinse out the stem. A few drops more of nitric acid are added to see whether more iodine is liberated. If so, it is again shaken out, and the extracts are united in the same test-tube. The volume is made up to 10 ml. with carbon tetrachloride, and the liquid is thoroughly mixed, then covered with a layer of water to prevent loss of carbon tetrachloride by evaporation, and set aside. A definite amount of each of the standard iodide solutions of two different concentrations—one of a higher and the other of a lower concentration than that of the unknown sample, as judged by the preliminary colour reaction—is placed in each of two separating funnels. Suitable strengths as standards for the comparison are 0·005 and 0·01 per cent. These standard solutions are then treated in exactly the same way as described above, and the carbon tetrachloride extracts are transferred to test-tubes and labelled. It is always desirable, but not essential, to take the same amount of the standard solutions as that of the unknown actually taken for the determination.

(*c*) *Colorimetric Comparison.*—One of the standard carbon tetrachloride extracts which seems to approximate closely to the unknown sample in depth of colour, is transferred from the test-tube to a matching cup, which is placed on the left-hand side of the colorimeter and set at 20 mm. The unknown extract is placed in another cup on the right-hand side, and the tints are matched in the usual way. The readings are noted, and the results are calculated in the usual way.

Table II gives the results of a few determinations of iodides in mixtures containing fluorides, chlorides, bromides and other salts, the composition of which is shown in Table I.

TABLE I

Composition of Mixtures of Halides taken for Determination

Other salts (sulphates, phosphates or nitrates of sodium, potassium, calcium and magnesium) were also added in various proportions to give a total volume of 100 ml.

	0·1 per cent. solution of potassium iodide or sodium iodide ml.	1·0 per cent. solution of sodium fluoride ml.	1·0 per cent. solution of sodium chloride ml.	1·0 per cent. solution of potassium bromide ml.
No. 1 mixture containing	8·8(KI)	10·0	20·0	15·0
No. 2 ,, ,,	12·6 ,,	10·0	25·0	20·0
No. 3 ,, ,,	15·8 ,,	15·0	30·0	20·0
No. 4 ,, ,,	3·0 ,,	20·0	10·0	10·0
No. 5 ,, ,,	12·0 ,,	15·0	10·0	5·0
No. 6 ,, ,,	25·5 ,,	15·0	10·0	10·0
No. 7 ,, ,,	19·5(NaI)	20·0	10·0	20·0
No. 8 ,, ,,	4·4 ,,	20·0	15·0	25·0
No. 9 ,, ,,	11·0 ,,	25·0	10·0	30·0
No. 10 ,, ,,	0·5 ,,	30·0	10·0	20·0

TABLE II

Results showing the Percentage of Iodides found in the Mixtures given in Table I

No.	Colorimeter reading of the unknown. Standard set at 20 mm.	Concentration of the standard Per Cent.	Amount found Per Cent.	Amount taken Per Cent.	Difference Per Cent.	Remarks
1.	22·6	0·01	0·00885	0·00880	0·00005	
2.	15·8	0·01	0·001265	0·00126	0·000005	
3.	12·5	0·01	0·0160	0·0158	0·0002	
4.	34·0	0·005	0·0030	0·0030	Nil	
5.	16·5	0·001	0·00121	0·00120	0·00001	
6.	15·5	0·01	0·0258	0·0255	0·0003	
7.	10·2	0·01	0·0196	0·0195	0·0001	
8.	34·0	0·005	0·00441	0·00440	0·00001	Standard set at 30.
9.	18·2	0·01	0·01099	0·0110	0·00001	
10.	35·5	0·0005	0·000493	0·00050	0·000007	Standard set at 35. 40 ml. solutions taken.

Our thanks are due to the Director of Public Health, Bihar and Orissa, for affording various facilities for carrying out this investigation in the Public Health Laboratories.

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Electrometric Analysis of Ferrous Sulphate Solutions

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WHEN compared with other methods of analysis of iron salts, electrometric titration has proved to be undoubtedly the best. It involves great difficulties, however, and I therefore thought it might be useful to investigate the properties of ferrous sulphate solutions themselves before I studied the action of *X*-rays upon them (*Phil. Mag.*, 1932, **14**, 198). As the results of these investigations have been described elsewhere (*J. of Gen. Chem., Russia*, 1931, **1**, 1012), I will only summarise them, and then draw some further conclusions from them.

Under the influence of atmospheric oxygen ferrous sulphate solutions are subject to spontaneous oxidation, and this process takes place more rapidly when the concentration of sulphate is high. In Table I is shown the percentage of the oxidation of pure sulphate solutions in 0·1 *M* sulphuric acid after a period of approximately 180 days.

TABLE I

Concentration Molar	Oxidation Per Cent.
0·001	2
0·01	8
0·98	28
0·107	45
0·45	72

Spontaneous oxidation takes place also in darkness, but at a slower rate. This oxidation proceeds with pronounced rapidity when platinum or platinum black is immersed in the solution (see Table II).

TABLE II

	4 Days Per Cent.	9 Days Per Cent.
0·1 molar without platinum	3	4
0·1 ,, with platinum	38	40
0·1 ,, ,, ,, black	85	100
0·001 ,, ,, ,, ,,	100	100

By taking into account the influence of the platinum, it is possible to develop a more perfect electrometric method. When a platinum electrode is being dipped into a solution containing ferrous sulphate an excess of ferric ions immediately begins to accumulate around it. To this is due the gradual increase in the oxidation-reduction potentials which always follows the use of a platinum electrode, and also an increase in the concentration of the ferric ions in solution.

It is obvious, therefore, that with a platinum electrode not the true potential, but a higher one, is being observed. The corresponding error depends on the period during which the platinum wire remains at the same place in the liquid; it will be smaller when this period is shorter, *i.e.* when the quantity of the ferric ions surrounding the wire is also small. It is also obvious that when the renewal of the adjacent layer of the solution takes place more rapidly, the apparent potential of the solution will approach more nearly to the true one. Therefore, checking the bilogarithmic curve, I had to use a fast-moving platinum electrode (the speed of the rotation was 100 to 600 R.P.M.). In this way I succeeded in proving that the bilogarithmic equation

$$\epsilon = \epsilon_0 + 0{\cdot}058 \log. \frac{C_3}{C_2} \quad .. \quad .. \quad .. \quad (1)$$

is quite correct at concentrations of ferrous ions between 99·9* and 0·002 per cent., especially in the right part of the curve. This result is more accurate than those obtained by other chemists.†

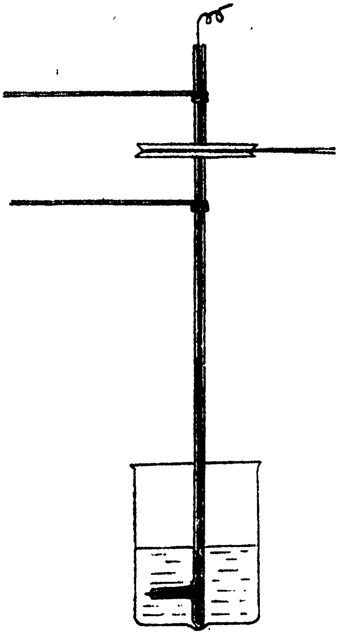

Fig. 1

In this way, by using a rotating platinum electrode (Fig. 1), it would be possible, by means of electrometric titration, to obtain results of a high degree of accuracy. Indeed, it may be possible to obtain very accurate data without titration, simply by measuring the oxidation-reduction potentials.

If the equation (1) is correct, it must be possible to determine the ferrous ion concentration C_2 (or ferric ions, *i.e.* $C_3 = 1 - C_2$) by the use of the inverse equation:

$$C_3 = \frac{10^{\frac{\epsilon-\epsilon_0}{b}}}{1 + 10^{\frac{\epsilon-\epsilon_0}{b}}}, \quad .. \quad .. \quad .. \quad .. \quad (2)$$

supposing b to equal 0·058; the value ϵ_0 may be found by interpolation; for instance, until the jump of the potential the course of the titration always remains independent of the concentration of sulphate, at least when the concentration ranges from 0·1 *M* to 0·001 *M*. (When the concentrations are lower the curves rise higher and the jump of the potential is less pronounced.) When, at a given concentration of the sulphate, the concentration of the sulphuric acid is increasing, the bilogarithmic curve is shifted downwards, parallel to itself. If we follow the course of this shifting at the middle point ϵ_0, which corresponds with the ratio of the concentrations $\frac{C_3}{C_2} = \frac{50 \text{ per cent.}}{50 \text{ per cent.}}$, the dependence of this E.M.F., ϵ_0, on the acid concentration may be represented by the curve (Fig. 2), where ϵ_0

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[*] I could not approach nearer the 100 per cent. concentration of ferrous ions, owing to the rapid oxidation of pure ferrous solutions immediately after their preparation.

[†] For instance, see Peters, *Z. phys. Chem.*, 1898, **26**, 193. The data which he obtained are included in the Landolt-Börnstein Tables (1929), as well as in all the books edited by Foerster, *Electrochemie wässeriger Lösungen*, including that edited in 1923. See also Fricke and Morse, *Phil. Mag.*, 1929, **7**, 134.

is measured against a normal calomel electrode. If, when working with oxidation-reduction potentials, sufficiently strong sulphuric acid* is used (*e.g.* 0·1 to 1·0*M*), the constant ϵ_0 will be determined with reasonable accuracy.

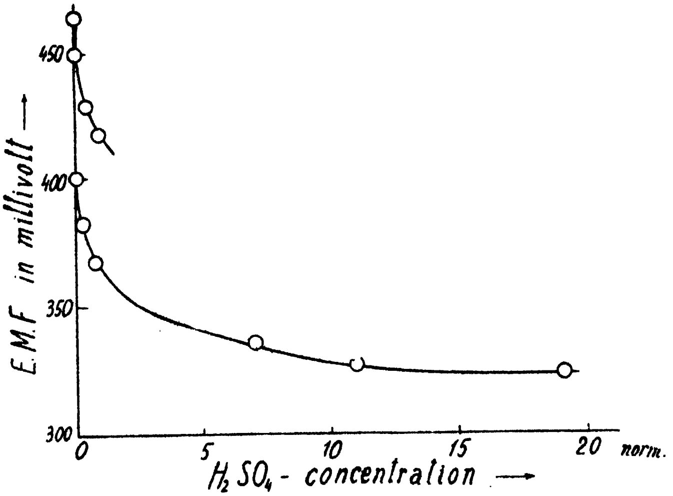

Fig. 2

As may be seen from Table III, the right-hand part of the bilogarithmic curve is very accurate. In the left-hand part, especially in the region of the more gradual course of the curve (40 per cent. to 80 per cent. Fe···), the accuracy may be increased by adding a definite quantity of potassium dichromate. This quantity must be such as to raise the ferric ion concentration to the region of highest sensitivity of the curve, for instance, to 97 to 98 per cent. Fe···. In this way, having two measurements of the oxidation-reduction potentials, the quantity of ferric ions present may be determined with an accuracy of about 0·1 to 0·2 per cent.† I should like to note also, that when, in accordance with modern theory, we substitute in the equation (I) for the concentration, the so-called "activities," *i.e.* if we write it in the form

$$\epsilon = \epsilon_0 + 0{\cdot}058 \log. \frac{C_3}{C_2} \cdot \frac{f_3}{f_2} \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

and compute these coefficients of activities f_3 and f_2, making use of the Debye-Hückel formula, it will be seen that, in the case of a change in the ratio of concentration, the correcting term $0{\cdot}058 \log. \frac{f_3}{f_2}$ does not change much. It has an effect only on the constant ϵ_0; for practical purposes this is of no importance, so that the old equation (I) still remains valid.

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* For electrometric titration more concentrated sulphuric acid is especially suitable, owing to its very pronounced jump (Hosteller and Roberts, *J. Amer. Chem. Soc.*, 1919, **41**, 1345).

† If the total quantity of iron in the solution is unknown, it will be sufficient to determine it by the addition of a known quantity of potassium dichromate, so that the prior and subsequent oxidation-reduction potentials both remain on the sensitive part of the bilogarithmic curve.

TABLE III

0·42 N Sulphuric Acid; $\epsilon_0 = 0{\cdot}380$ Volt

Oxidation-reduction potential V	Ferric sulphate, calculated Per Cent.	Ferric sulphate, found Per Cent.
0·3047	4·79	4·88
0·3498	23·58	23·18
0·3727	42·80	42·08
0·3925	62·16	60·94
0·4160	80·68	80·06
0·4581	95·69	95·64
0·4631	96·45	96·24
0·4709	97·36	97·20
0·4852	98·49	98·38
0·4992	99·13	99·16
0·5213	99·79	99·74

It is thus seen that when a rapidly rotating platinum electrode is employed, the old bilogarithmic equation (I) is correct at concentrations of ferrous ions between 99·9 and 0·002 per cent. It is thus possible to obtain very accurate results without titration, simply by measuring the oxidation-reduction potentials. In such a way the percentage of ferric ions present may be determined with an accuracy of about 0·1 to 0·2 per cent. The total quantity of iron in the solution may be determined by adding a small quantity of potassium dichromate and measuring the oxidation-reduction potentials before and after the addition.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A QUALITATIVE REACTION FOR THE DETECTION OF LIGNONE SULPHONATES (SULPHITE WASTE LIQUOR)

WASTE liquor from the manufacture of cellulose pulp by the sulphite process has come to be a constituent, legitimate or otherwise, of very varied commercial products. Either crude or after some simple "processing," it is found in such diverse materials as fireproof cements and tanning liquors. Its detection is sometimes important. A very easy and fairly sensitive qualitative test has been used in this laboratory for ten years, but only lately was the fact brought to my notice that, though the reaction involved has no novelty, its utility for the detection of the lignone sulphonates has not been elsewhere noted. It has here been found that a convenient *modus operandi* is as follows:—About 10 ml. of a filtered aqueous extract of the material under examination are warmed with 0·5 g. of potassium chlorate till the reagent is dissolved. The solution is cooled and cautiously acidified with hydrochloric acid (sp.gr. 1·20), of which 10 ml. or more should ultimately be added. If a lignone sulphonate (the characteristic constituent of sulphite waste liquor) is present, a marked orange-red colour will develop on warming. If the amount present is great enough, an orange-red solid, which has a gummy consistence when hot, will separate as the reaction proceeds. At the same time there is usually a considerable evolution of gas. The red colour is easily distinguished from the yellow which would be produced by the mutual action of potassium chlorate and hydrochloric acid alone. The insoluble chlorine compound which is formed in the above reaction seems to be the same as that noted by Seidel and Hanak (*Mitteilung aus dem Technischen Gewerbe Museum*, Wien, 1897, 7, 283; Abst. *J. Soc. Chem. Ind.*, 1898, 17, 596), as well as by subsequent observers.

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SOME CHARACTERISTICS OF "LIMONITES" USED IN THE CURE AND PREVENTION OF BUSH SICKNESS

FOR the past three years Whangarei (Ruatangata) limonite, introduced by Aston as an economical cure for bush sickness in stock in the Rotorua district of New Zealand, has been used with unfailing success. For some reason, however, limonites from different deposits in New Zealand have been found to differ very markedly in their efficacy as a cure for bush sickness, and the present investigation was undertaken to correlate, if possible, the chemical properties of these limonites with the field tests.

Chemical analysis of the efficacious Ruatangata and Okaihau ores and the relatively ineffective Onekaka and Puhipuhi ores showed that, in addition to iron oxide (62·30–71·25 per cent.), silica and water, the following elements were present in small amounts in some or all of the ores:—Titanium, calcium, magnesium, manganese, phosphorus, sulphur, barium, sodium and potassium, together with traces of copper, chromium, arsenic, antimony, nickel and cobalt.

A further analysis of 21 samples, derived from four different deposits, showed that in most cases the commercial samples found by field trials to be ineffective in curing bush sickness were low in combined water and contained appreciable amounts of calcium carbonate. With one exception, the ores contained less than 1·0 per cent. of ferrous oxide.

Although solubility experiments with dilute hydrochloric or dilute oxalic acid solution showed no striking correlation with the field evidence, it was found that, in the presence of reducing agents, under certain conditions the effective limonites were from twice to four times as soluble as the ineffective samples. It was found with an acetic acid and sodium acetate solution (*p*H 4·0), in which the limonite samples are insoluble, that the amount of iron dissolved at equilibrium was directly proportional to the amount of sodium hydrosulphite added (as reducing agent) and practically independent of the nature of the limonite. It was shown, however, that the rate of solution of the iron in the acetic acid and sodium acetate buffer solution (*p*H 4·0) containing 1·25 per cent. of sodium hydrosulphite was much greater with the effective samples—a fact suggesting that the curative value of the ores was to be correlated with the rate of solution of the iron in acid-reducing agents rather than with the total solubility of the iron at equilibrium.

As a general method of differentiation between limonite samples, a sugar hydrochloric acid reagent was used. This reagent was prepared by dissolving 100 g. of commercial sucrose in 1 l. of *N*/10 hydrochloric acid made up with freshly-boiled distilled water. In the solubility test 0·5 g. of limonite and 50 ml. of the reagent were placed in a 200-ml. conical flask, which was immediately stoppered with a tightly-fitting cork provided with a Bunsen valve to protect the solution from oxidation by air. The flask was shaken in boiling water for 15 minutes, and the solution was then quickly cooled, made up to 100 ml. with water, and immediately filtered through a No. 42 Whatman paper. After approximately 20 ml. of the filtrate had been collected, the funnels and filter papers were removed to exclude the possibility of further solution of the limonite, and a suitable aliquot portion was taken for the determination of the iron.

Heating tests showed no striking change of solubility in sugar hydrochloric acid unless the sample had been heated above 550° C. Fineness of grinding, as determined by sieving tests, was not found to have any appreciable effect upon the solubility of the ore in the sugar hydrochloric acid reagent.

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THE ACIDS OF CIDER

THE barium salts of tannic and citric acids are practically insoluble in 20 per cent. (by vol.) alcohol; those of malic and succinic acids are soluble in 20 per cent. alcohol, but insoluble in 75 per cent. alcohol; and the barium salts of lactic and acetic acids are soluble in 75 per cent. alcohol.

Malic acid is the chief acid of apple juice; it is fermented to lactic acid. According to the equation for this fermentation 134 parts of malic acid (= 150 of tartaric acidity) give 90 parts of lactic acid (= 75 of tartaric acidity). Citric acid is said to be present in apple juice, but my tests have given negative results. Succinic acid, a metabolic product of yeast, is present in all fermented drinks, forming about 0·5 per cent. of the sugar fermented; the quantity in cider will therefore be small. Acetic acid is formed by acetification of alcohol.

The fermentation of the malic acid follows the primary alcoholic fermentation, and is most noticeable in sharp highly nitrogenous juices. These undergo a very rapid alcoholic fermentation and soon go dry; then in quite a short time the original acidity may have been more than halved. In order to prevent cider sickness, it is inadvisable at any time to let the acidity of the cider sink below 0·5 to 0·55 per cent. (as tartaric acid). Hence, it is often necessary to make a small addition of acid even to pure juice. Tartaric, citric, lactic, and even acetic acid have been used, the price of malic acid, so far, being prohibitive. If such juices are diluted to moderate the rate and extent of the alcoholic fermentation, the need for an addition of acid will be obvious.

The following figures indicate the nature of the changes taking place in samples of apple juice fermented in the laboratory at room temperature.

Weeks	Acidity Per Cent.	Malic acid (as tartaric acid) Per Cent.	Lactic acid Per Cent.	Acetic acid Per Cent.
0	1·23	1·03	(0·23)	—
2	1·14	0·79	0·09	0·04
6	0·86	0·48	0·35	0·05
10	0·81	0·37	0·41	0·14
0	1·11	0·96	(0·15)	—
2	0·95	0·69	0·18	0·01
6	0·53	0·14	0·54	0·04
*10	0·54	0·09	0·60	0·06
0	0·92	0·71	(0·24)	—
4	0·46	0·12	0·53	0·04
10	0·50	0·13	0·53	0·09

* The same juice hydrolysed gave: malic acid, 0·09; lactic acid, 0·76; and acetic acid, 0·06 per cent.

A small amount of "malic" acid persists even in cider vinegar, whilst lactic acid diminishes as cider ages. Titration of an old sample of cider vinegar gave 5·03 per cent. of acidity (as acetic acid), and the vinegar contained 5·04 per cent. of acetic, 0·18 per cent. of lactic, and 0·08 per cent. of malic acid.

In sub-acid and slow-fermenting juices the alcoholic and malic fermentations occur simultaneously, and such juices may even show lactic acid production from sugar. In a cider cellar the above changes take place more slowly, owing to the lower temperature, and they can be moderated by various means. The following are figures for typical examples of commercial ciders:

Grade	Acidity Per Cent.	Malic acid (as tartaric acid) Per Cent.	Lactic acid Per Cent.	Acetic acid Per Cent.
A (P.J.)	0·64	0·20	0·26	0·30
B (P.J.)	0·63	0·15	0·43	0·22
C (N.M.)	0·50	0·13	0·36	0·10
D (N.M.)	0·57	0·13	0·45	0·08
E (D.)	0·62	0·13	0·17	0·11

None of these samples contained added acid except sample E, a draught cider with 0·29 per cent. of tartaric acid. (The 20 per cent. alcohol cannot quite be relied on to exclude tartrate.)

I. *Acetic Acid.*—One hundred ml. of cider are heated to incipient boiling and then transferred to a steamed-out distilling flask, 100 ml. of water, containing 3 ml. of *N* sulphuric acid are added, 100 ml. are distilled, and the distillate is titrated with *N*/10 sodium hydroxide solution, phenolphthalein being used as indicator. Of the acetic acid present, 36·6 per cent. distils.

II. *Lactic and Acetic Acids.*—Twenty ml. of the cider are neutralised with a saturated solution of barium hydroxide in a 110-ml. measuring flask (phenolphthalein as indicator). Two ml. of 10 per cent. barium chloride solution and about 81·5 ml. of industrial methylated spirit (74 O.P.) are added, and the liquid is cooled, again neutralised, and made up to 110 ml. with water. After standing for 3 hours at 15 to 18° C., it is filtered through a dry filter. (Any excess of barium hydroxide should be precipitated by means of a current of carbon dioxide and the liquid re-filtered.) From 75 ml. of the filtrate most of the alcohol is evaporated, 2 ml. of a 10 per cent. solution of anhydrous sodium sulphate are added, and the residue is dried and ignited. It is then warmed for 5 minutes on the water-bath with 20 ml. of *N*/10 hydrochloric acid in a covered vessel, and titrated back with *N*/10 sodium hydroxide solution. (Ml. $\times \frac{110}{75} \times 5$) gives the lactic and acetic acid per 100 ml. of cider in terms of *N*/10, and the acetic acid equivalent is subtracted to obtain the lactic acid.

III. *Malic, Lactic and Acetic Acids.*—Fifty ml. of cider are neutralised with barium hydroxide solution in a 100-ml. measuring flask, and then treated with 5 ml. of barium chloride solution and 20 ml. of alcohol (74 O.P. spirit), diluted, cooled, and made up to 100 ml. after being again neutralised. The mixture is allowed to stand for 3 hours, and then filtered, and 25 ml. of the filtrate are treated as described above. (Ml. × 4 × 2) gives the equivalent of the acetic, lactic and malic acids. The malic acid is obtained by difference. The operations are carried out at 15° to 18° C.

If in (II) the total acidity (as tartaric acid) in the cider exceeds about 0·8 per cent., less than 20 ml. of the cider must be taken.

In (III) the actual percentage of malic acid in the cider must not exceed 0·5, 0·4 and 0·3 per cent. if the alcohol-content of the cider is 0, 5 and 10 per cent., respectively; otherwise less than 50 ml. must be taken.

On the Continent a similar test is used for lactic acid in wine, but is not considered accurate if the sugar-content exceeds 0·5 per cent. Sugar does appear to increase the apparent lactic acid figure a little; hence, so far as possible, my results have been obtained with dry samples.

The following results were obtained with experimental mixtures:

Taken	Per Cent.	Found	Per Cent.
		At 16° C.	
Sucrose	2·0		
Invert sugar	8·0		
Malic acid	0·2	Malic acid	0·19
Lactic acid	0·35	Lactic acid	0·37
Tannin	0·15	At 25° C.	
Malic acid	0·19	Malic acid	0·14
Lactic acid	0·40	Lactic acid	0·45
Tannin	0·15	At 20° C.	
Malic acid	0·19	Malic acid	0·20
Lactic acid	0·43	Lactic acid	0·44

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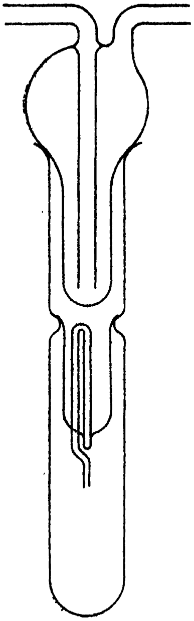
A MICRO-EXTRACTION APPARATUS



THE body of the apparatus is a tube, 6 in. long and 1 in. in diameter, the top being either flanged, or flanged and ground, to take a pear-bulb condenser, and the bottom closed as in a boiling tube. The actual extractor consists of a cup, 1½ in. long and ⅝ in. wide, with a syphon tube attached to the bottom and a flanged top to support it on three projections about 3½ in. from the bottom of the outside tube. The internal diameter of the syphon tube must be not less than 2 mm., or capillary attraction will cause it to syphon continuously. The pear-bulb condenser rests on the flanged top of the outside tube and extends down to within about ½ in. of the top of the extractor cup. When the apparatus is heated over a water-bath steam is apt to condense on the outside of the condenser and run into the apparatus. This can be prevented either by fitting the condenser with a ground-glass joint through the centre of which is a central vent, or by taking steps to keep the steam away from the apparatus. The latter method is recommended, as it obviates unnecessary complication of the apparatus and is quite easily and effectively carried out by keeping the bath covered and preventing the steam from escaping from between the inner ring and the apparatus by means of a disc of cardboard, or, better still, of metal, with a centre hole cut to fit the apparatus closely.

The method of heating is immaterial, but whatever method is employed, it is wise to have at least the outer tube constructed of resistance glass, such as Pyrex.

The apparatus holds about 10 ml. of solvent, and when the extraction is complete, the cup can be lifted out by the syphon tube with a thin wire hook and the solution can then be poured out easily without the slightest loss. There is a

Whatman's extraction thimble, 10 × 50 mm., which is of a convenient diameter for use in this apparatus, but is slightly too long. This can be cut down to the required length.

The volatile solvents in general use for hot extraction in the Soxhlet apparatus have been tested and found to work satisfactorily. With chloroform the apparatus syphons about 20 to 25 times an hour, and with ether slightly faster. Extraction is rapid, as it takes place at the b.p. of the solvent. One hour's extraction of phenacetin and caffeine tablets with chloroform gave a result only 0·05 per cent. below that obtained by three hours' extraction in the same apparatus, and these times compare very favourably with those taken by a larger extractor.

The apparatus will be found particularly useful in the analysis of tablets and pills from which it is necessary to remove the excipient, for the determination of non-volatile resins, etc., in vegetable tissue, and for the usual fat-extractions, and it has the advantages of being small, easily cleaned and requiring only small amounts of sample and solvent. It has been found that gentle and even boiling can best be obtained by putting a small glass bead into the outer tube with the solvent.

Arrangements have been made for this extractor to be obtained from Messrs. Baird & Tatlock, Ltd., at the price of 8s. 6d.

I wish to thank Mr. G. S. Stevens for his co-operation.

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A RAPID MICRO-BROMIDE TEST FOR THE DETECTION OF LINSEED OIL IN MUSTARD SEED OIL

The insoluble bromide test, originally devised by Hehner and Mitchell (Analyst, 1898, **23**, 310), has been used in most of the Public Health Laboratories in Bengal in the analysis of mustard-seed oil under the Bengal Food Adulteration Act. Mustard-seed oil, which is extensively consumed as an edible oil throughout India, particularly in Bengal, is frequently adulterated with linseed oil. Toms (Analyst, 1928, **53**, 71) has devised a rapid micro-gravimetric method of determining the halogen absorption of oils and fats by exposing a film of the oil, derived from a single drop, on a weighed microscope slide in an atmosphere of bromine. While studying this "bromine vapour" method, it occurred to me that possibly a rapid qualitative test for the detection of linseed and other highly unsaturated fatty oils might be based on the behaviour of the brominated film when treated with ether and petroleum spirit (in which the mixed bromo-glyceride is almost insoluble), and experiments in this direction have given promising results. Considerable information may be gained at the outset by an examination of the physical condition of the brominated film, as was first suggested by Toms (*loc. cit.*). Thus, linseed oil and its distinctive fatty acids (linolenic acids) yield hard, colourless gritty films with wrinkled surface, whereas mustard-seed oil gives a soft, opaque and glossy film, without any tendency to wrinkle.

One drop of the oil (0·04 to 0·06 g.) is spread on a microscope slide (which must be free from grease) in a uniform film by drawing the narrow edge of a second microscope slide slowly along the whole length of the first slide at an angle of 30°. The slide is then exposed to an atmosphere of bromine for 20 to 25 minutes, after which it is left in the air for a short time to remove the excess of bromine.

After the physical appearance of the brominated film has been noted, the slide is placed horizontally on the edge of a small rectangular glass trough and covered with a mixture in equal parts of ether and petroleum spirit. The film is then stirred with a very thin glass rod and examined for the appearance of any white, curdy precipitate, the whole of the slide being meanwhile kept covered with the mixed solvents. From the amount of flocculent precipitate (dilinolenic-linolic bromo-glyceride) an estimate may be formed of the quantity of linseed oil (or other oil yielding insoluble bromides) in the sample.

Ten samples of mustard-seed oil, tested in this way, gave no indications of a white, curdy precipitate; cotton-seed, arachis, kapok, and mowrah oils also gave negative results.

Abundant precipitates were obtained with linseed oils, boiled linseed oil, double-boiled linseed oil and fish oil. Mixtures of linseed oil with 5 to 50 per cent. of mustard-seed oil gave precipitates, the amounts of which were approximately proportional to the quantity of linseed oil present.

A mixture of 90 per cent. of cotton-seed oil with 10 per cent. of linseed oil showed a perceptible precipitate, but 2 per cent. of linseed oil could not be detected. Mustard-seed oil adulterated with 5 per cent. of linseed oil showed a considerable amount of precipitate, and with a 50 per cent. mixture the whole of the precipitate was practically insoluble in the mixed solvents.

Work is in progress with the object of making the test more strictly quantitative.

I wish to thank Rai J. N. Ghosh Bahadur, Chairman, District Board, Khulna, for facilities for working in the Board's laboratory, and Dr. M. M. Bose, Public Analyst and District Health Officer, for his keen interest and valuable suggestions throughout the work.

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THE EFFECT OF VARYING STORAGE CONDITIONS ON THE DETERIORATION OF ERGOSTEROL

It is well known that ergosterol is liable to deteriorate on storage. Mention of this was made by Bacharach, Smith and Stevenson (Analyst, 1933, **58**, 128), but the only quantitative work bearing on this subject, so far as we are aware, is that done by Callow (*Biochem. J.*, 1931, **25**, 79), who reported the rate of gain in weight when ergosterol was stored in air over a dehydrating agent.

We have found it necessary, in connection with the large-scale manufacture of this material, to determine the change in specific rotation and m.p. during storage, and the results of our tests are given here.

Except where otherwise stated, each determination of the specific rotation was carried out as follows:—A 2 per cent. w/v solution of ergosterol was made, without the application of heat, in chloroform answering the requirements of the B.P., 1932. The rotation was observed in a 100-mm. or 200-mm. jacketed tube at 20° C. with sodium light. The specific rotation was calculated from the mean of about 10 readings made from 10 to 20 minutes after complete solution had been effected. The maximum variation from the mean reading was 0·02°, so that the error in the specific rotation recorded is less than 1·0 (100-mm. tube) or less than 0·5 (200-mm. tube).

In the determination of the m.p. the procedure of the B.P., 1932, was followed, the actual m.p. being the final temperature recorded.

Preliminary Experiments.—Prior to carrying out the keeping tests it was thought desirable to discover the effects produced on the optical rotation by varying the general procedure, outlined above, for preparing the solution, the length of time the solution was allowed to stand prior to examination, the type of chloroform used, the concentration, and the temperature at which the rotation was determined. These results are given in Table I.

TABLE I

	Sample	Specific rotation $[\alpha]_D$		Remarks
1. Effect of heat during preparation of solution.	A.	−122·3°	(100 mm.)	average of 6 determinations.
		−115·0	(100 mm.)	heated almost to b.p.
		−116·5	(100 mm.)	,, ,, ,, ,,
	B.	−126·4	(100 mm.)	average of 4 determinations.
		−121·0	(100 mm.)	heated almost to b.p.
	C.	−129·1	(100 mm.)	average of 5 determinations.
		−129·4	(100 mm.)	heated to 50° C. for 5 minutes.
2. Effect of standing in solution.	C.	−129·1		See above.
		−127·8	(100 mm.)	5 hours at lab. temp. in clear glass bottle.
		−114·9	(100 mm.)	24 hours at lab. temp. in clear glass bottle.
	D.	−128·5	(100 mm.)	
		−113·0	(100 mm.)	24 hours at lab. temp. in clear glass bottle.
	B.	−126·4		See above.
		−103·0	(100 mm.)	48 hours at lab. temp. in clear glass bottle.
3. Effect of concentration.	A.	−122·3		See above.
		−122·0	(100 mm.)	1 per cent. w/v solution.
4. Effect of temperature.*	E.	−118·5	(100 mm.)	old solution $t=16$° C.
		−117·0	(100 mm.)	,, ,, $t=20$° C.
		−114·0	(100 mm.)	,, ,, $t=25$° C.
		−111·0	(100 mm.)	,, ,, $t=31$° C.
		−109·0	(100 mm.)	,, ,, $t=37$° C.
Effect of solvent and temperature.*	F.	−131·3	(200 mm.)	B.P. $CHCl_3$ $t=15$° C.
		−129·8	(200 mm.)	B.P. $CHCl_3$ $t=20$° C.
		−127·0	(200 mm.)	B.P. $CHCl_3$ $t=25$° C.
		−131·7	(200 mm.)	Freshly distilled alcohol-free $CHCl_3$ $t=15$° C.
		−130·0	(200 mm.)	,, ,, $t=20$° C.
		−127·5	(200 mm.)	,, ,, $t=25$° C.
		−126·5	(200 mm.)	alcohol-free $CHCl_3$ 4 days old (contains phosgene) $t=15$° C.
		−124·2	(200 mm.)	,, ,, $t=20$° C.
		−120·0	(200 mm.)	,, ,, $t=25$° C.

* Uncorrected for expansion of solvent. This would account for a fall in specific rotation, for values between −110° and −130°, of 0·7° to 0·8° per 5° C. rise in temperature.

It was proved, therefore, that heating during the preparation of the solution and standing in solution should be avoided; that the temperature must be carefully controlled; that slight variations in the concentration have no appreciable effect; and that chloroform B.P. is preferable to "purified" chloroform, for the small amount of alcohol it contains has a negligible effect on the rotation, but prevents the production of abnormally low results caused by a partly-decomposed solvent.

Keeping Tests.—Optical determinations on stored samples were all carried out as described under the general procedure above, the 200-mm. tube being used. The material was stored either in amber glass bottles in the dark (marked "dark" in Table) or in clear glass bottles in diffused daylight (marked "light" in Table).

In the tests in which an atmosphere of nitrogen was used, the ergosterol was stored in 2-oz. bottles fitted with a rubber bung through which passed a glass tube reaching to the bottom of the bottle. The stopper being slightly loosened, nitrogen was passed into the bottle through the glass tube for several minutes and the bottle gently shaken. The rubber bung was then tightly secured, the supply of nitrogen stopped, and the entrance-tube closed. The nitrogen used was commercial cylinder-nitrogen containing less than 1 per cent. of oxygen.

The results are given in Table II.

In view of the figures of Tanret (*vide* Callow), Callow (*loc. cit.*), and Bacharach, Smith and Stevenson (*loc. cit.*), samples C, H, and J may be considered normal samples of commercial ergosterol of good quality. G is somewhat inferior.

TABLE II

	Conditions of storage						
Sample	Container, etc.	Atmosphere	Temperature	Period	Specific rotation $[\alpha]_D$	Melting-point °C.	Colour
C.	See Table I				−129·5°	162·8–163·2	
	dark	air	38° C.	7 weeks	−127·7		
	dark	nitrogen	38° C.	7 weeks	−129·6		
	light	air	lab.	7 weeks	−127·2		
	light	nitrogen	lab.	7 weeks	−128·5		
	dark	air	lab.	7 weeks	−128·5		
	dark	nitrogen	lab.	7 weeks	−130·0		
	dark	air	5° C.	7 weeks	−128·3		
	dark	nitrogen	5° C.	7 weeks	−130·2		
J.					−127·7		
	dark	air	lab.	17 weeks	−125·5		
C.	dark	air	38° C.	22 weeks	−105·5	141·5–145·0	strong yellow
	dark	nitrogen	38° C.	22 weeks	−113·7	146·0–151·0	pale yellow
	light	air	lab.	22 weeks	−126·5	159·2–160·0	slight yellow
	light	nitrogen	lab.	22 weeks	−126·0	159·5–160·2	slight yellow
	dark	air	lab.	22 weeks	−126·5	160·5–160·8	slight yellow
	dark	nitrogen	lab.	22 weeks	−127·2	160·7–161·2	slight yellow
	dark	air	5° C.	22 weeks	−126·2	161·6–162·1	pract. white
	dark	nitrogen	5° C.	22 weeks	−127·0	162·0–162·4	pract. white
H.					−128·2		
	dark	air	lab.	36 weeks	−124·5		
C.	dark	air	38° C.	52 weeks	− 65·2	133 −138	strong orange
	dark	nitrogen	38° C.	52 weeks	− 97·0	138 −148	strong orange
	light	air	lab.	52 weeks	−111·0	145 −153	mod. yellow
	light	nitrogen	lab.	52 weeks	−102·2*	134 −147*	yellow*
	dark	air	lab.	52 weeks	−119·2	154·5–156·0	mod. yellow
	dark	nitrogen	lab.	52 weeks	−122·2	158·0–159·5	mod. yellow
	dark	air	5° C.	52 weeks	−125·0	161·3–162·1	slight yellow
	dark	nitrogen	5° C.	52 weeks	−126·4	161·3–162·3	very sl. yellow
G.					−122·5		
	dark	air	lab.	3 years	−108·2		

* Very small sample; consequently, large surface exposed.

The figures in Table II, expressed as fall in specific rotation in degrees per week and fall in melting-point in degrees per week under the various conditions, are given in Table III.

TABLE III

	7 weeks	17 weeks	22 weeks		36 weeks	52 weeks		3 years	
Conditions	(spec. rotn.) $[\alpha]_D$	(spec. rotn.) $[\alpha]_D$	(spec. rotn.) $[\alpha]_D$	m.p. °C.	(spec. rotn.) $[\alpha]_D$	(spec. rotn.) $[\alpha]_D$	m.p. °C.	(spec. rotn.) $[\alpha]_D$	Sample
Dark, air, 38° C.	0·26	—	1·09	0·83	—	1·23	0·48	—	C.
Dark, nitrogen, 38° C.	0·01 gain‡	—	0·72	0·56	—	0·63	0·29	—	C.
Light, air, lab.*	0·33	—	0·14	0·15	—	0·35	0·20	—	C.
Light, nitrogen, lab.*	0·14	—	0·16	0·13	—	0·52†	0·31†	—	C.
Dark, air, lab.*	0·14	—	0·14	0·11	—	0·20	0·14	—	C.
Dark, air, lab.*	—	0·13	—	—	0·10	—	—	0·09	G.H.J.
Dark, nitrogen, lab.*	0·07 gain‡	—	0·10	0·09	—	0·14	0·07	—	C.
Dark, air, 5° C.	0·17	—	0·15	0·05	—	0·09	0·02	—	C.
Dark, nitrogen, 5° C.	0·10 gain‡	—	0·11	0·04	—	0·06	0·02	—	C.

* The tests were begun in September, and consequently the test-periods up to 36 weeks had a temperature-range of about 15° to 20° C. For the 1-year and 3-year periods the upper temperature-limit was about 30° C.

† See above.

‡ Probably due to slight initial dehydration.

Thus the substitution of nitrogen for air, storage in the dark and low temperatures reduce the rate of, though they do not entirely prevent, deterioration. Under these conditions an increase in rate of deterioration does not apparently occur with longer standing. With change of temperature from 5° C. to 15° C. the effect is not very marked, but it is considerable with further rise of temperature.

Our main object in this work was a consideration of deterioration during bulk storage, *i.e.* with quantities of at least 5 kg., and not with small quantities which could readily be stored in sealed glass tubes. Deterioration under these latter conditions has been dealt with elsewhere (*cf.* Callow, *loc. cit.*).

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Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

WHEAT ACT, 1932. LIABILITY OF CERTAIN CONSIGNMENTS OF IMPORTED "MIDDLINGS" TO QUOTA PAYMENTS

R. and W. Paul, Limited *v.* Wheat Commission

On January 18th the Court of Appeal (Master of the Rolls, Lords Justices Slesser and Romer) delivered judgment on the appeal by the defendants against the judgment of Mr. Justice Roche (*cf.* Analyst, 1934, **59**, 406).

The learned Judge had held that:

(i) Bye-law No. 20 was *ultra vires* and therefore the jurisdiction of the Court was not ousted in favour of arbitration. The defendants claimed that the Act and Bye-laws thereunder made provision for the final determination by arbitration of disputes arising in such matters as might be specified in the bye-laws.

(ii) The thirteen consignments in question were not "flour" as defined in the Wheat Act, but were "wheat offals" as defined in the Wheat Act, and therefore exempt from quota payment, and the plaintiffs were entitled to recover the sum of £1,912 5s. 2d., which had been paid as quota payments, and to a declaration of non-liability for payment where such payments had not yet been made.

(iii) The plaintiffs could not recover the money paid on the first three consignments, as the action had not been brought within six months. The defence of the Public Authorities Protection Act was entitled to succeed.

The Wheat Commission appealed against the findings adverse to it, and the plaintiffs made a cross-appeal against that part of the judgment based upon the Public Authorities Protection Act. Sir William Jowitt, K.C., and Mr. H. Hull appeared for the Wheat Commission, and Sir Leslie Scott, K.C., and Mr. J. Whyatt for the plaintiffs.

The Master of the Rolls, giving judgment, said that, in his view, the jurisdiction of the Court was not excluded in favour of arbitration. The claim of the plaintiffs appeared to lie outside the ambit of any arbitration required by the Wheat Act, 1932. As regards the proper construction to be placed upon the Wheat Act and the result of the sections and definitions and rules derived therefrom, he said: "A miller or importer cannot escape the liability to quota payments by treating or using the resultant product of milling as offals, however small may be the amount of flour extracted from the wheat milled. The purpose of milling is to produce flour, not offals. Offals are residual products, and unless the products contain not more than 7½ per cent. of the parcel in the form of flour or other non-residual, the product is or is to be deemed flour. It is argued that under the definition of wheat offal, if the residual product, after some flour has been extracted, is intended for animal or poultry food, then although this residual may be rich in flour, it is none the less offal, and the liability to make quota payments does not attach to it. I cannot agree to this." He further indicated that his own construction of the Act led to a different conclusion from that of Mr. Justice Roche in the Court below, and it required an examination of the parcels to be made so as to determine whether they were within the latitude and consequent exemption allowed to offals. In respect of the liability of the consignments in question he said: "From the evidence as a whole I am satisfied that all these consignments were produced by stopping the milling of flour before it had passed to its normal conclusion. They are not offals or residual products extracted in the process of milling wheat. With great respect to the learned Judge, I have come to the conclusion that all these parcels are subject to the quota payments, with the result that on this point the judgment must be reversed, and the plaintiffs' claim for repayment of the £1,912 5s. 2d. dismissed with costs."

Upon the cross-appeal the Judge was right in holding that the Public Authorities Protection Act applied to protect the defendants. The cross-appeal must be dismissed with costs.

Lord Justice Slesser read a judgment agreeing that the appeal should be allowed and the cross-appeal dismissed.

Lord Justice Romer, in the course of his judgment, said: "The plaintiffs have failed to show that any of the consignments in question can properly be described as wheat offals and their action should have been dismissed." In his opinion the appeal must be allowed and the cross-appeal dismissed.

The appeal was allowed with costs, and the cross-appeal dismissed with costs.

Leave to appeal to the House of Lords was given.

SALE OF DRIED ALFALFA AS TEA*

In this case the United States Attorney of the Northern District of Illinois, acting upon a report by the Secretary of Agriculture, asked for seizure and condemnation of 51 packages of dried alfalfa at Chicago, Ill., alleging that the article had been shipped in inter-state commerce from California, and charging adulteration and misbranding in violation of the Food and Drugs Act. The article was labelled "——American Vegetable Tea Orange Pekoe Type Green."

Analysis of a sample by the U.S.A. Department of Agriculture showed that it consisted of dried alfalfa. It was alleged in the charge that the article was adulterated in that dried alfalfa had been substituted for tea of the Orange Pekoe type, which the article, by reason of the labelling, purported to be.

Misbranding was also alleged under the provisions of the Act relating to drugs, in that the labelling of the article bore unwarranted curative and therapeutic claims, as "a tonic in nutritional and secondary anaemia, general blood impoverishment, dietary deficiencies, malnutrition and gastro-intestinal disturbances, and debilitated states," etc.

On June 15th, 1933, no claimant having appeared for the property, judgment of condemnation and forfeiture was entered, and it was ordered by the Court that the product be destroyed by the United States Marshal.

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* U.S.A. Dept. of Agriculture. Food and Drug Administration. Notices of Judgment under the Food and Drugs Act. No. 21199. Issued August, 1934.

EFFECTS OF TRICHLOROETHYLENE

An inquest was held on January 6th at Birmingham on the body of a man who had died suddenly on December 8th. He had been employed by a firm at Smethwick in degreasing plated cycle handlebars by means of trichloroethylene contained in a machine of special construction which had been in use since 1932. The solvent in the iron tank of this machine was converted into a heavy vapour, which condensed upon the handle bars placed inside and freed them from grease.

The works manager said that men on night duty were allowed to smoke while at work, and he had not been aware that Imperial Chemical Industries, Ltd., had issued regulations in which there was a warning against smoking when working with a degreasing machine in which trichloroethylene was used. He had since been informed that if the vapour were inhaled through a cigarette, there was a possibility of its being converted into phosgene.

Mr. B. P. Crawshaw, who designed the machine in question, said that there had been four deaths in Germany, from trichloroethylene poisoning, but not in connection with a degreasing plant. In his opinion it was perfectly safe to use the machine, and there were a large number of them working in this country.

Dr. J. C. Bridge, Senior Medical Inspector of Factories to the Home Office, said that there had been four or five deaths in England through using trichloroethylene, and information on the subject had been published in the Chief Inspector's Annual Report (*cf.* Analyst, 1934, **59**, 626).

Mr. H. Shaw, an industrial chemist, Imperial Chemical Industries, Ltd., said that trichloroethylene had been in use for degreasing for about ten years. It could have acute effects if taken in quantity, but there was no evidence that small doses could poison a man. Two years ago Imperial Chemical Industries, Ltd., having made tests, warned the owners of degreasing plants not to allow smoking. If air containing 0·1 per cent. of trichloroethylene vapour were drawn through a cigarette, the temperature of the lighted end being about 600° C., the air inhaled would contain about 3 parts per million of phosgene. In reply to a question as to what was a fatal dose of phosgene, Mr. Shaw said that he thought that it was 25 parts per million. Rats subjected to trichloroethylene vapour over a period of six months had shown no signs of poisoning; in fact, they had increased in weight.

Dr. Whitelaw, pathologist, said that he could discover no natural cause of death.

Professor Haswell Wilson, of Birmingham University, said that there was no evidence of gaseous poisoning, but that there was paralysis of the respiratory centre. He could find no evidence that death was due to a natural cause, but attributed it to paralysis of the respiratory centre caused by some poisonous substance. Trichloroethylene poisoning by inhalation could be excluded, and there was no evidence of acute or chronic phosgene poisoning.

The jury found that death was due to natural causes.

Agricultural Research Council

REPORT FOR THE PERIOD, JULY, 1931, TO SEPTEMBER 30TH, 1933*

THIS Report, covering the first two years of the Council's existence, gives a survey of the state of agricultural science in Great Britain in the years 1931 to 1933, and also describes the activities of the Council, with its Committees and Sub-Committees, during that period.

After a preliminary introduction, outlining the functions of the Council and its relations with the Medical Research Council and the Department of Scientific and Industrial Research on the one hand, and, on the other, with the Agricultural Departments and the Development Commission, the Report describes its procedure, and the nature of the subjects assigned to its six Standing Committees.

Part II (pp. 13–20), dealing with the Economic Outlook, discusses *inter alia* the policy of "controlled industry," and the application of economic principles, including the theory of prices, to agricultural practice.

Part III, on SOIL (pp. 21–43), opens with an introduction on the nature of soil, and this is followed by a section on Soil Physics, in which an outline is given of the physical work carried out at Rothamsted from 1913 to the present time.

The "sticky point value," suggested by F. Hardy, has been subjected to critical examination by Keen and others, and it has been shown that the percentage of moisture in a thoroughly kneaded mass of soil which is just sufficiently moist to stick to the fingers or a knife is related, in the case of calcium clay soils, to the colloidal complex of the soil.

A second promising method, recently devised at Rothamsted by Schofield and Scott Blair, aims at ascertaining the "heaviness" of a soil in the agricultural sense; and in normal soils, where heaviness is correlated with clay-content, it indicates the amount of clay present. The method consists in ascertaining the weight which must be applied to a thin cylinder of moist soil in order to cause elongation; the test is made in a specially designed machine termed a pachimeter.

Soil Biology.—An outline is given of the work done by three Departments at Rothamsted since 1908. It has recently been shown by Cutler that there are organisms quite distinct from those described by Winogradsky, which share in the formation of nitrates.

SOIL CHEMISTRY.—Although no sharp distinction can be made, broadly it would be true to say that, whilst the Rothamsted studies aim at relating soil to plant-growth, the Scottish and Welsh investigators have had as their main purpose the study of the soil itself. As one result of these studies it may be claimed that it is now possible to begin the work of classifying British soils on a satisfactory basis.

With regard to soil reaction it is pointed out that, whilst the *p*H value has been shown to be a very useful figure for comparing the lime status of soils of similar origin, and the requirements of crops growing in similar climates, it does not follow that a series of *p*H values compiled to show the relative tolerance of crops to acidity in, *e.g.* the English Midlands, would hold good for soils in north-east Scotland.

Advances in the theories of soil reaction and base exchange have thrown new light on changes occurring in experimental plots at Rothamsted. Superphosphate was long suspected of increasing soil acidity, but the history of the Woburn plots has proved the suspicion to be unfounded. Long-continued applications of superphosphate to this soil, naturally deficient in lime, have not reduced the quantity of exchangeable bases. At Rothamsted, again, base-exchange theory provided Page with an explanation of the very serious damage suffered by clay soils when flooded by sea-water.

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* Report to the Committee of the Privy Council for the Organisation and Development of Agricultural Research, 1934, pp. 205. Cmd. 4718. To be purchased from H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 3s. net.

The relative proportions of silica to alumina, and of silica to alumina and ferric oxide, in the different soil horizons, depend both on the parent material and upon the degree of weathering; hence, climate has been adopted in many countries as the chief factor in classifying soils. In the cool humid climates of Northern Europe the molecular SiO_2/Al_2O_3 ratio may be 3 : 1 in the upper soil horizons; in the lower, ratios of 2 : 1 might be expected. In arid countries ratios of 5 or 6 : 1 may be found, and in the humid tropics ratios of less than 2 : 1 are common. The conclusions of Robinson on the ratios of Welsh soils, and those of Crowther on American soil ratios are discussed in the report.

Reference is made to the mineralogical analyses of soils by Hendrick and Newlands and by Hart. Even from the small number of soils (60 to 70) hitherto reported on, it may be inferred that, whereas in England and Wales study of the soil's "clay fraction" provides information of the kind most useful to the farmer, in the case of the northern Scottish soils, in which the "clay fraction" is always small, the nature and conditions of the minerals present in the "fine-sand fraction" call for further study by those who endeavour to assess the soil's agricultural value.

The chemistry of the soil's organic matter has been continuously studied at Rothamsted and Bangor, but the problem of the origin of humus has not yet been finally solved. An outline is given in the Report of the evidence for and against the lignin theory put forward by Page. The fate of fresh organic matter in soil and the causes that lead to its loss are now being investigated by Crowther and his colleagues at Rothamsted.

Soil Surveys and Soil Mapping.—A Soil Correlation Committee, set up by the Department of Agriculture, has so far identified and described about 150 soil series in England and Wales, and about 80 in Scotland. Each "soil series" recognised by the Committee includes within it all soils essentially similar in respect of parent material, mode of formation, topographical position and drainage conditions. The soil series are further subdivided into classes according to their texture. All the conditions responsible for a soil series are reflected in the soil's profile, or section, and the profile, which is studied either in natural sections or by boring with an auger, is therefore the unit to which the surveyor's attention is now mainly directed in the field.

Institutes for Soil Research.—A description is given of the history and activities of the Rothamsted Experimental Station and of the Macaulay Institute for Soil Research at Aberdeen.

PLANTS.—The Introduction to Part IV (pp. 44–77) summarises the improvements effected in plants, including wheat and fruit trees, by scientific breeding, and points out that breeding for resistance to disease is one of the most promising lines of work, although methods of direct attack or prevention, such as spraying, must long remain part of the necessary routine of the farmer and gardener. The workers at Rothamsted are studying the general aspects of the virus problem, and are in constant touch with the investigators of the Medical Research Council, who are dealing with virus diseases in animals and human beings.

The later part of this section gives a survey of the investigations now in progress at various institutions and research stations on plant physiology, plant breeding, horticulture, and fruit research, the virus diseases of plants and other diseases, and the improvement of grass-land.

Part V (pp. 78–87) is concerned with Animal Heredity and Genetics, and Part VI (pp. 88–97) with Animal Nutrition and Physiology. An outline is given of the work being done at the Rowett Research Institute, Aberdeen, and at the Cambridge Institute for Animal Nutrition. Part VII (pp. 98–156), on the Diseases of Animals, describes the development of research in Great Britain during the early part of the present century, and then gives an outline of further advances in the field of animal pathology made by British workers. This is classified under the names of the various diseases, and concludes with a bibliography containing 59 references.

DAIRY RESEARCH (Part VIII, pp. 157–166).—With only limited funds at the disposal of the Council, it was held necessary to restrict Dairy Research Institutes to problems likely to yield results either of fundamental theoretical interest or of practical economic importance. Recent researches of most importance from the dairying point of view include the work that has shown the high nutritional value of young grass, and the need by cattle of a balanced ration containing both vitamins and mineral salts. The causes of loss of cows from dairy herds have been studied at various institutes; the average length of the milking life of cows works out at the surprisingly low figure of about 4 years. Other points investigated include the cost of production of "ordinary" and "special" milk, the physiology (including the genetics) of dairy cattle, the inheritance of milking properties, and statistical studies of the factors controlling the yield and quality of milk.

Reference is made to the fact that since 1931 evidence has been accumulating to show the value of the determination of the freezing-point as a test for the adulteration of milk with water.

Much discussion has taken place on the subject of the relative value of raw and pasteurised milk (*cf.* Report of the Committee of the Economic Advisory Council on Cattle Diseases. H.M. Stationery Office, Cmd. 4591).

Details are given of the work that has been done and is in progress at the Dairy Research Institutes.

PART IX (AGRICULTURAL ENGINEERING, pp. 167–173) deals with the work that is being done at the Institute for Research in Agricultural Engineering at Oxford, where agricultural machinery is tested and problems such as those connected with crop drying are investigated.

PART X (pp. 174–178) gives a description of the use of STATISTICAL METHODS at various Research Institutes, and the Report ends with a Conclusion by the Chairman of the Agricultural Research Council (the Rt. Hon. Lord Richard Cavendish). Appendix I gives the Charter creating the Agricultural Research Council; Appendix II is a note on administrative arrangements; Appendix III gives the personnel of the Committees of the Council; Appendix IV gives a summary of the grants sanctioned by the Council. There are three indexes—the first of personal names, the second of Government Departments, Institutions and other bodies, and the third of scientific subjects.

Union of South Africa

DEPARTMENT OF AGRICULTURE

ANNUAL REPORT OF THE CHIEF OF THE DIVISION OF CHEMISTRY FOR THE YEAR ENDED JUNE 30TH, 1933

IN his Annual Report Dr. St. J. C. O. Sinclair, F.I.C., gives an outline of the work carried out by the Division of Chemistry. In addition to its work for the Department of Agriculture, the Division also undertakes, as part of its regular routine, chemical work for the Departments of Public Health, Justice, Finance (Customs and Excise) and Mines and Industries. In addition, the Division is charged with the conduct of soil surveys required by the Department of Irrigation. The Division maintains three institutions—at Pretoria, Johannesburg and Capetown, respectively—and is also concerned with the work of the chemical sections of the four schools of agriculture.

PASTURE PROBLEMS.—*Feeding Value of Grasses of the Digitaria Species.*—At Pretoria the Division collaborated with the Division of Plant Industry in investigations relating to the feeding value of certain grasses (*Digitaria* species) at various stages of growth, and an account of the results has been published as a bulletin (*Science Bull.*, No. 126, by D. J. R. van Wyk). The most outstanding result of the experiments is that the young grass is relatively rich in phosphoric oxide and protein, irrespective of the progress of the season. On the other hand, the grass growing undisturbed alongside diminishes in P_2O_5 and protein as the season progresses. The phosphoric oxide figure is always much less in the mature dead grass than in the young grass, varying generally between one-half and one-third of the amount in the latter. In the best grass the amount seldom exceeds 0·5 per cent., which is very low. The lime-content increases as the plants mature, and seems to bear no relation to the P_2O_5-content. The crude protein is always greatest in the young plants, as usual. Most grasses reach values of over 10 per cent., but under 13 per cent. Extreme values of 3 per cent. are reached when the grass is dead. The following are typical analyses of samples of three species:

	Moisture in air-dried material Per Cent.	Percentages on dry sample							
		Ash	Fibre	Carbo-hydrates	Ether extract	P_2O_5	CaO	Protein	True protein
Digitaria Polevansii	7·8	6·90	36·8	46·2	1·3	0·27	0·50	8·8	5·5
D. littoralis	8·5	11·1	38·5	38·7	1·3	0·40	0·87	10·4	6·3
D. geniculata	8·2	10·9	36·3	44·0	2·1	0·35	0·77	6·8	5·8

UNIT VALUES OF CONSTITUENTS OF FERTILISERS AND FARM FOODS.—For a number of years the costs of fertilisers and farm foods have been discussed in an article in the July issue of *Farming in South Africa*, and each year the tests are brought up to date.* The system of valuation is fully explained in an article by Mr. C. O. Williams, published in the Journal of the Agricultural Department.†

In calculating these unit values it is assumed that insoluble phosphoric oxide has half the value of the soluble phosphate in any particular class of fertiliser, and the assumption agrees fairly well with the actual market price of the fertilisers. The values of the water-soluble and citric-soluble phosphate in superphosphate are taken to be equal—an assumption that agrees with the market value for citric-soluble phosphate in other fertilisers. For bone fertilisers the assumption is only approximately correct, and it is also true that this insoluble phosphate becomes available in the soil more readily than the insoluble phosphate in such fertilisers as superphosphate or basic slag. The system of unit values applied to farm foods is based on the "carbohydrate" value, in which the proteins and the fat are both reckoned at two-and-a-half times the value of the soluble carbohydrates, together with an allowance of 2s. 6d. per unit of phosphoric oxide and 6d. per unit of lime for residual manurial value in foods rich in these constituents.

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* See *Bulletins: Division of Chemistry Series*, No. 126, for 1933, and No. 133, for 1934 (by A. J. Taylor), from which the details abstracted here have been taken.

† Reprints can be obtained from the Division of Chemistry, Pretoria.

New Zealand

ANNUAL REPORT OF THE DOMINION LABORATORY

In this, the Sixty-seventh Annual Report, the Dominion Analyst (Mr. W. Donovan, M.Sc., F.I.C.) gives a summary of the analyses and investigations undertaken for the different Government Departments. Of the 5345 samples examined at the main laboratory in Wellington, 3279 were for the Health Department. The totals for the branch laboratories were: Auckland, 2647; Christchurch, 2568; Dunedin, 1663. Most of these were milks submitted by the Health Department. The greater part of the work done for the police consisted in the examination of exhibits in cases of suspected poisoning, but it also included the analysis of materials in connection with criminal investigations.

Alcohol in Urine.—A sample of urine received in connection with a death from suspected alcoholism contained 0·52 per cent. (by vol.) of alcohol. This was considered to indicate that the deceased died from alcoholic poisoning.

Arsenic in Exhibits derived from Glass Bottles.—Traces of arsenic in certain exhibits were found, after extensive investigation, to be derived from the glass of the bottles in which the material had been collected.

Counterfeit Coins.—An interesting investigation was made in connection with the manufacture and uttering of counterfeit coins. Analyses showed that uttered coins and some found in the accused's house were of the same composition. The accused denied that the uttered coins had been made by him, but comparison of enlarged photographs of both sets of coins showed that they had all been made in the same mould. The accused was convicted.

Bread with "Reduced Starch."—Samples of bread advertised as "Starch reduced—Protein increased" were examined. This bread was sold in loaves weighing not more than 1 lb. 9 oz., as against 2 lb. for ordinary bread, but owing to the fact that they had a greater volume in proportion to their weight than ordinary bread, the loaves looked heavier than they really were. In the preparation of the bread a certain proportion of flour from which starch had been washed was mixed with ordinary flour. The bread contained slightly less starch than some of the ordinary white bread on the market, but the advantage of this is doubtful. The protein present was 11·3 per cent. by weight, calculated on the dry material. Straight-run flours contain from 9 to 15·1 per cent. of protein on the dry basis. Hence, by using selected flour, bread containing considerably more protein than 11·3 per cent. could be made in the ordinary way, if desired. From a dietetic point of view this special bread would not be superior to average well-made ordinary white bread.

"Bread Improvers."—Several so-called "bread improvers" were examined and found to contain mineral salts. Bakers were warned against the use of such "improvers," which are not permitted by the New Zealand regulations.

PYRETHRUM FLOWERS GROWN IN NEW ZEALAND.—Samples of flowers from pyrethrum (*P. cineriaefolium*) grown in the North Auckland District were tested for their insecticidal value by determining the pyrethrin-content. Flower-heads grown from the Dalmatian variety of pyrethrum contained 0·33 per cent. of pyrethrins, and a specimen from the Japanese variety contained 0·74 per cent. The Japanese variety has been introduced into America, where it is growing successfully, and could no doubt be grown in New Zealand.

POISONOUS PRINCIPLE OF RAGWORT.—Preliminary work has been undertaken with a view to isolating and characterising the chemical nature of the poisonous principle in ragwort (*Senecio jacoboea*). About 0·15 per cent. of an alkaloid in the crude state was isolated from the air-dried plant. Large quantities are now being separated, in order to make physiological tests on the pure alkaloid and to study its chemical nature and properties. It is not definitely known whether the alkaloid is actually responsible for the poisoning of stock by ragwort.

KAURI-GUM.—The standardised resin obtained by the solvent process worked out in the Wellington laboratory is in the form of a dry granular powder, entirely free from foreign material. Reports received from European manufacturing firms who were supplied with bulk samples indicate that a ready market awaits the purified gum. Specimens of various grades of crude kauri-gum have been investigated as to their solubility and behaviour when subjected to the purifying process. Experiments on the esterification of the pure material are proceeding. Samples of resin associated with lignitic coal from Otago and Southland were found to be kauri-resin of high melting-point. The extent of the resin-bearing beds should undoubtedly be determined.

ANTIMONY IN ENAMELWARE.—As the result of reports from Great Britain of certain cases of antimony poisoning due to the use of enamelware in preparing an acid drink, it was thought advisable to examine the various brands of such ware sold locally, and especially kitchen utensils intended for use in the storage, preparation or cooking of foods. With several brands dangerous amounts of antimony were dissolved from the enamel by acid foods.

PITTING OF COPPER IN CONTACT WITH RUBBER AND KEROSENE.—A corrosion problem was investigated for the post and telegraph department. The copper anode of a transmitting valve cooled by circulating kerosene was found to be badly pitted where it was in contact with a rubber washer. The kerosene was discoloured, but sulphur and acidity were low. A sample from the tank, after stirring, contained 0·0081 per cent. of suspended matter, in which was 0·0052 per cent. of inorganic matter. This contained some copper, but much more zinc, showing that the copper salts formed by corrosion of the copper anode had attacked the galvanised coating of the tank. Corrosion tests showed that the kerosene became very dark when heated in contact with copper and pieces of the rubber washer. The copper was covered with a black deposit, and badly pitted. The discoloured kerosene also had the same effect on a copper sheet over which it was allowed to flow. On testing rubber from a washer of good quality in the same way, it was found that the kerosene was only slightly discoloured, the deposit on the copper was much smaller, and there was no pitting. It was clear that rubber of poor quality was the cause of the corrosion. Although copper catalyses the oxidation of rubber, rubber of good quality, preferably containing anti-oxidants, should be fairly resistant.

Standard Specifications for Solvents

THE British Standards Institution has issued specifications for the following eight industrial solvents:

Dibutyl phthalate (No. 573)
Diethyl phthalate (No. 574)
Carbon tetrachloride (No. 575)
Glacial acetic acid (No. 576)
Hexachloroethane (No. 577)
Technical acetic acid (No. 578)
Technical ether (No. 579)
Trichloroethylene (No. 580)

These specifications, which have been drawn up by the technical committee of the Chemical Division of the B.S.I., under the chairmanship of Dr. J. Vargas Eyre, prescribe tests and limits for specific gravity, acidity, alkalinity, distillation, etc., these limits having been fixed after consultation and agreement with the principal manufacturers and users of the solvents.

Copies of the specifications may be obtained from the Publications Department of the British Standards Institution, 28, Victoria Street, London, S.W.1. Price 2s. 2d. each, post free.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Bromates in Flour. **J. Kulman.** (*Z. Unters. Lebensm.*, 1934, **68**, 375–377.)—The flour is mixed with chloroform and centrifuged. The upper layer of flour is then removed, the bromate being deposited on the bottom of the tube. If necessary, further quantities of the flour may be added and the process repeated until the residue of bromate becomes appreciable. The bromate is then reduced with nascent hydrogen to bromide, which is detected by means of the red tetrabromofluorescein formed with an acid solution of fluorescein and a

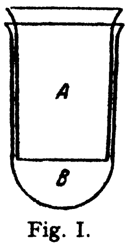

Fig. I.

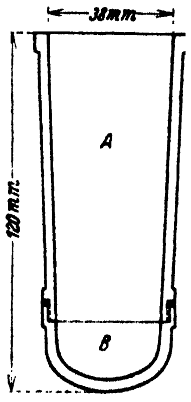

Fig. II.

drop of chlorine water (*cf.* Baines, ANALYST, 1928, **53**, 178). The method is applicable only when the bromate is present as crystals in the flour. For the centrifuging it is convenient to use a tube B (Fig. I) into which is ground a sleeve A. The flour may then be removed with B, the bromate and chloroform collecting in A.

For the determination of the bromate, use may be made of a bronze centrifuge tube constructed in two parts, A and B (Fig. II); these are screwed together, with a rubber jointing inserted. Forty g. of the flour and 75 ml. of carbon tetrachloride are centrifuged for 5 minutes (2000 to 2500 r.p.m.). With very fine flour, traces of the bromate may not separate; the centrifugation is then repeated. The lower part B is unscrewed and its contents transferred, with the help of carbon tetrachloride, to a glass-stoppered Erlenmeyer flask, and then filtered through asbestos moistened with the tetrachloride in a Gooch crucible. The residue on the filter is freed from fat by washing with 30 to 50 ml. of carbon tetrachloride and then returned to the Erlenmeyer flask, the walls of which are rinsed down with 30 ml. of water. After addition of 10 ml. of 2 per cent. potassium iodide solution and 10 ml. of 10 per cent. hydrochloric acid, the closed flask is left for 5 minutes. Five ml. of starch paste are added, and the liquid over-titrated with 0·01 *N* thiosulphate solution and back-titrated with 0·01 *N* iodine solution; 1 ml. of 0·01 *N* thiosulphate ≡ 0·28 mg. of potassium bromate. In presence of persulphate or iodate, a separate portion of the flour is treated and the persulphate determined either iodimetrically or colorimetrically; iodate is determined as in edible salt. Details of the procedure will be given later. T. H. P.

Flavine in White Wines. L. Genevois. (*Bull. Soc. Chim.*, 1934, **1**, 1504–1505.)—White wines exhibit a faint white fluorescence, which is readily observable in ultra-violet rays (Wood's lamp), and is attributed partly to the presence of flavine and its photo-derivative, lumiflavine. Zymoflavine, obtained from bakers' yeast either by extraction with methylal or by autolysis, cannot be extracted from its aqueous solution by hydrocarbons or their chloro-derivatives, which cause no reduction in the fluorescence of the liquid. Extraction of a white wine (from the Bordeaux district) with trichloroethylene, however, yielded an extract which, after filtration, showed a faint blue fluorescence and, on distillation, left a fluorescent solution. Three such extractions removed all this fluorescent substance. The residue of the wine was then treated by Kuhn's method for the detection of flavine: when the liquid was made alkaline, exposed to the light of a mercury-vapour lamp for 45 to 60 minutes, rendered acid again, and extracted with trichloroethylene, a fluorescent extract was obtained. Hence, there seems no doubt that the wine contained a flavine in small amount. That the substance extracted from the non-irradiated wine by trichloroethylene is identical with lumiflavine is, however, not yet proved. T. H. P.

Detection of Margarine and Hardened Oils in Foodstuffs. J. Grossfeld and J. Peter. (*Z. Unters. Lebensm.*, 1934, **68**, 345–358.)—The use of coconut butter and similar fats in margarine has greatly diminished in Germany, and the best way of recognising margarine is by means of the hardened oils (iso-oleic acid) it contains. Such oils may be detected in edible fats by the following semi-micromethod: 500–550 mg. of the fat are boiled for 10 minutes in a 50-ml. Erlenmeyer flask under a reflux condenser with 5 ml. of alcoholic potash (40 ml. potassium hydroxide solution of sp.gr. 1·5 and 40 ml. of water, made up to 1 l. with 95 per cent. alcohol). The resulting soap solution is treated with 20 ml. of alcoholic lead acetate solution [50 g. of crystallised lead acetate, 5 ml. of 96 per cent. acetic acid, and 80 per cent. (vol.) alcohol to 1 l.], 1 ml. of 96 per cent. acetic acid and 3 ml. of water, the precipitate formed being dissolved by heating under a reflux condenser. After the corked flask has been left at about 20° C. for 2 hours, the precipitate is collected on a small glass-filter crucible (Schott & Gen. 10G/3), washed with 11 to 12 ml. of 70 per cent. (vol.) alcohol (previously used to rinse out the Erlenmeyer flask), and finally pumped as dry as possible.

The crucible and precipitate, with the filter-disc uppermost, are transferred to a suitable extraction apparatus; 0·6 ml. of 96 per cent. acetic acid is poured on to the disc and, with use of the Erlenmeyer flask, extraction with 20 ml. of the lead acetate solution is continued until the precipitate is dissolved. The boiling should be so vigorous that part of the liquid spurts into the extraction space and so facilitates the solution. The hot liquid is treated with 2 ml. of cold water and energetically shaken, any precipitate forming being dissolved by a short heating under a reflux condenser. After the flask has been left corked for 2 hours the precipitated lead salts of the fatty acids are again collected on the glass crucible, washed with about 12 ml. of 70 per cent. (vol.) alcohol and pumped as before. The crucible and precipitate are returned to the extraction apparatus, and the precipitate is dissolved in 20 ml. of a boiling mixture of 95 per cent. alcohol and 96 per cent. acetic acid in equal volumes. The hot solution of the lead salts is transferred to a 400-ml. Erlenmeyer flask, together with 10 ml. of the alcoholic-acetic acid mixture used for rinsing. The iodine value of the solid fatty acids is then determined as follows:—The cold lead salt solution is mixed with exactly 20 ml. of about 0·2 *N* iodine (25·4 g. of iodine dissolved in 96 per cent. alcohol to 1 l.), and the liquid then shaken with 200 ml. of water. After a few minutes the excess of iodine is titrated with 0·1 *N* thiosulphate solution. The iodine used up by a mixture of 15 ml. of 96 per cent. acetic acid with 15 ml. of 95 per cent. alcohol is determined similarly and used as a correction. (1 ml. of 0·1 *N* thiosulphate ≡ 14·12 mg. of iso-oleic acid.)

The above procedure includes two crystallisations of the lead salts, but a single crystallisation usually suffices to indicate the probable presence or absence of hardened fats and the consequent advisability of carrying out the double-crystallisation process. The limiting percentages (means in brackets) of iso-oleic acid found in edible fats with one crystallisation of the lead salts were: 2 hard fats, 24·8 to 38·8 (31·8); 9 margarine-fats, 9·3 to 17·0 (13·1); 11 butter-fats, 0·7 to 2·1 (1·6); 6 pigs'-fats, 1·5 to 2·0 (1·9); 5 ox-fats, 1·6 to 2·5 (2·2); 3 mutton-fats, 2·8 to 3·2 (2·9); cocoa butter, 1·3. When the lead salts were crystallised twice, the corresponding percentages were: 20·5 to 35·4 (28·0); 4·1 to 9·9 (7·3); 0·6 to 1·4 (0·9); 0·1 to 0·4 (0·3); 0·5 to 1·5 (1·1); 1·3 to 1·6 (1·5); 0·3.

Experiments with cocoa butter show that an addition of more than 10 per cent. of hardened fat is indicated by the increase in the iso-oleic acid value when the lead salts are crystallised only once. With two crystallisations, 1 to 2 per cent. of the hardened fat gives a distinct rise in the iso-oleic acid figure. The natural content of iso-oleic acid in butter-, beef-, and mutton-fats disturbs the test only if more than 20 per cent. of butter-fat or more than 10 per cent. of beef- or mutton-fat is present in a mixture with cocoa butter. T. H. P.

Taint Production in the Fat of Chilled Beef. C. H. Lea. (*J. Soc. Chem. Ind.*, 1934, **53**, 391–392T.)—Deterioration of flavour in chilled beef-fat may be produced by micro-organisms, by odour absorption, or by oxidation. In the first case the rise in acidity, which almost invariably accompanies the deterioration in flavour, varies considerably owing to the different abilities of the organisms to hydrolyse fat. In samples taken from chill-rooms of retail shops a free acidity of 1·02 (as percentage of oleic acid) in one sample was associated with a worse flavour than an acidity of 1·36 per cent. in another, whilst in yet another sample the acidity was as high as 5·73 per cent., although there were no visible organisms. Visible mould was present in two samples with acidities of 10·51 and 13·71 per cent. An inoculation of fat from the interior of blocks of fresh beef scrotal fat with *Mucor* spores (a strain taken from mouldy beef-fat), produced a progressive rise in acidity in one case from 0 to 10·4 per cent. in 1 day, and in another to 10·4 per cent. in 16 days. Appreciable oxidation of chilled beef-fat stored in air does not generally occur unless there is undue exposure to light, but the use of carbon dioxide atmospheres has made storage practicable for much longer periods. However, after long periods bleached greyish or white patches may occur on the external fat of quarters, apparently owing to the conversion of oxyhaemoglobin into methaemoglobin, and all such samples examined had higher peroxide oxygen values than adjoining fat of normal appearance. D. G. H.

Some Indian Acorn Oils. S. V. Puntambekar and S. Krishna. (*J. Indian Chem. Soc.*, 1934, **11**, 721–726.)—The oils were extracted from the acorns of three of the 30 or more species of oak grown in India, *Quercus incana* Roxb., *Q. dilatata*, Lindl., and *Q. ilex*, Linn. The oil from the acorns of *Q. incana* was investigated in detail, since this is probably the most common and best known of all the species. The kernels (81 per cent.) were dried, and 16 per cent. of oil was extracted from them by means of petroleum spirit. The oils from the species of acorns examined were liquid, that from *Q. incana* was yellow, and those from the other 2 species were orange. The following analytical figures were obtained:—(*a*) *Q. incana*; (*b*) *Q. dilatata*, and (*c*) *Q. ilex*:—Sp.gr. at 25° C., (*a*) 0·9081, (*b*) 0·9084, (*c*) 0·9079; $n_D^{30^\circ}$, (*a*) 1·4576, (*b*) 1·4588, (*c*) 1·4576; saponification value, (*a*) 192·2, (*b*) 188·4, (*c*) 189·9; iodine value (Hanus), (*a*) 81·5, (*b*) 90·3, (*c*) 83·0; acetyl value, (*a*) 14·8, (*b*) 21·1, (*c*) 17·4; Hehner value, (*a*) 96·1, (*b*) 88·2, (*c*) 94·9; acid value, (*a*) 13·0, (*b*) 22·2, (*c*) 8·5; unsaponifiable matter, (*a*) 0·8, (*b*) 2·3, (*c*) 0·9 per cent. The solid and liquid acids from the oil of *Q. incana* were separated by Twitchell's method, and their methyl esters fractionally distilled. They contained palmitic, 17·1; lignoceric (?), 0·9; and oleic acid, 82·0 per cent. The acetate of the purified sterol, separated from the unsaponifiable matter, melted at 126°–128° C., and appeared to be derived from sitosterol. D. G. H.

Malt Analysis. British and Continental Methods and the Inter-Relationship of Results. R. H. Hopkins, H. Lloyd Hind, and F. E. Day. (*J. Inst. Brewing*, 1934, **40**, 445–451.)—To convert the results of malt analysis by the Institute of Brewing Committee method (*id.*, 1933, **39**, 517) into the results which would be obtained by the usual Continental methods, *i.e.* Salzburg Convention for moisture, extract and colour and the Windisch–Kolbach method for diastatic power (see *Brewers' J.*, 1930, 237) the following calculations may be used: —Moisture, add 0·23 per cent.; extract, multiply by 0·802; colour, multiply by 0·086; diastatic power, multiply by 3·50, and then subtract 16. The respective standard errors of these figures are ±0·12, 0·005 and 0·008, the value for diastatic power being an approximation only. The factor for the extract converts English "lbs. per quarter" into the Convention units "per cent. Plato"; the Plato unit of a wort is the number of g. of wort-solids contained in 100 g. of wort, the relationships between sp.gr. and solids which hold for cane sugar being adopted for the purposes of a standard. This is considered preferable to the Balling unit. Variations in the ratio of the extracts determined by the two methods are attributed to the moisture-contents, and it is presumed that if the moisture exceeds 5 per cent., the malt will be inadequately ground in the Institute mill. The results were obtained experimentally with a wide range of malts, prepared according to English and Continental malting methods, but only two malts made from Californian barley and two from six-rowed barleys were included. Since the latter have a high grain-volume the Institute method for extract must give spuriously high results for them, and spuriously low results for malts made from two-rowed barleys; the Convention method avoids these errors. The essential points of difference between the two methods are indicated in each case. The Pollak–Egloffstein method for the determination of diastatic power has not been included in the comparisons, as it takes into account both the dextrinolytic and saccharifying components of diastase. Previous results (*J. Inst. Brewing*, 1934, **40**, 247) have shown that the Convention method of mashing gives, on an average, 0·08 to 0·15 per cent. more permanently-soluble nitrogen than the Institute method. J. G.

Analysis of Acriflavine, B.P. and Neutral Acriflavine. G. F. Hall and A. D. Powell. (*Quart. J. Pharm.*, 1934, **7**, 522–530.)—If the solubility requirements of the B.P. for acriflavine are to be satisfied, the product must contain not only the pure hydrochloride of 2 : 8-diamino-10-methyl acridinium chloride, but also an appreciable percentage of diamino-acridine hydrochloride. In confirmation of the results of Gailliot (*id.*, 1934, **7**, 63), 30 per cent. of the latter compound has been found to be necessary, although large quantities are undesirable. In any case, the present official limit test is unsatisfactory, and improvements are therefore suggested as follows :—*Qualitative.*—The formaldehyde test of the B.P. responds to proflavine, which is diamino-acridine sulphate; it requires the presence of sulphuric acid, and then gives a precipitate both with 90 per cent. acriflavine and with diamino-acridine. It is preferable (cf. *New and Non-Official Remedies*, 1930, p. 151) to add a few drops of a solution of formaldehyde and 5 ml. of a 10 per cent. solution of sodium nitrite to 5 ml. of 0·4 per cent. (w/v) test solution, and to filter after 5 minutes. The filtrate is red if acriflavine is present (distinction from euflavine and diamino-acridine compounds). This is more sensitive than the test in which an effervescence with sodium bicarbonate is taken as an indication of the presence of acriflavine, and it may be adapted as a test for euflavine if this is first converted into acriflavine by the action of hydrochloric acid. *Quantitative.*—A solution of 0·5 g. of the sample in 20 ml. of water (30 ml. with neutral acriflavine) is neutralised with 0·1 *N* sodium hydroxide, with bromothymol blue as indicator. It is then diluted to 35 ml. and warmed to 60° C., and 25 ml. of the alkali are added, followed by 20 g. of sodium chloride. The precipitate is separated on a glass crucible on the following day, and is washed with 5-ml. portions of saturated sodium chloride solution at 5° C., until 5 ml. of washings require not more than 0·05 ml. of 0·1 *N* sulphuric acid to neutralise it to thymol blue. A mixture of the total filtrate and 26 ml. of the 0·1 *N* acid is boiled, cooled, and titrated with 0·1 *N* sodium hydroxide solution, with thymol blue as indicator (each ml. of alkali neutralised ≡ 0·0282 g. of diamino-acridine dihydrochloride). Precipitation as ferricyanide (*cf.* Powell and Hall, *Quart. J. Pharm.*, 1933, **6**, 389) is recommended for the determination of the "total flavines" (*i.e.* the total methylated and unmethylated derivatives of diamino-acridine) since it avoids the difficulty of the possible presence of nitrogenous decomposition-products. Gailliot's method (*loc. cit.*), which involves precipitation of the base with silver oxide, and subsequently, of diamino-methyl acridinium iodide with potassium iodide, is considered unsatisfactory. The following limits appear desirable:—"Total flavines" (as acriflavine), not less than 95·0 per cent.; unmethylated compounds (as diamino-acridine dihydrochloride), not more than 20·0 per cent.; Cl as acriflavine, not less than 95·0 per cent.; identification by the proposed colour test. J. G.

Analysis of some Mercurial Ointments. W. R. Heading. (*Quart. J. Pharm.*, 1934, **7**, 406–412.)—Existing methods are surveyed. In general, extraction of mercury with acid involves prolonged boiling to ensure that it is complete, and the disadvantages of extraction of the base material in organic solvents are losses due to protracted shaking and to the solubility of mercury salts in the solvent, and the difficulty of filtration of the finely-divided residue. The following procedures are suggested:—*General Method.*—A known weight of the sample is dissolved in 5 ml. of warm xylene or petroleum spirit in a dry round-bottomed centrifuge tube (1·9 × 10 cm.); the preparation should not come within 25 mm. of the top of the tube. The mixture is centrifuged until the supernatant layer is clear, and this is removed with a syphon, and the process is repeated with 3 further 8-ml. portions of petroleum spirit followed by 5 ml. of 90 per cent. alcohol. The residue is treated as follows:—For *Unguentum Hydrargyri*, *Ung. Hydrarg. Compositum*, *Oculentum Hydrarg. Oxidi*, and all ointments containing uncombined oxides of mercury.—The alcohol should have been drawn off to within 12·5 mm. of the suspension; the remainder is then removed by evaporation, the residue is dissolved in warm nitric acid, the solution being transferred to a flask and titrated with 0·05 *N* sodium thiocyanate as in the official assay of yellow mercuric oxide; the amount of sample taken should be equivalent to 0·15 to 0·2 g. of metal. For *Ung. Hydrarg. Ammoniatum.*—The moist residue obtained from 1 to 2 g. of sample is transferred to a flask, and the tube is rinsed with alcohol or acetone, followed by 3 ml. of a 10 per cent. solution of potassium iodide. The official assay for ammoniated mercury is then carried out after addition of 3 g. of potassium iodide. With *Ung. Hydrarg. Subchloridi*.—The moist residue obtained from 0·75 to 1·5 g. of sample is treated as described for ammoniated mercury, with the omission of potassium iodide, and the official assay for subchloride of mercury is completed; it should not be necessary to add more than 30 ml. of 0·1 *N* iodine solution. The advantages are economy of time (an assay can be completed in 25 minutes) and material, and avoidance of fumes of acid or of hydrogen sulphide. The percentage errors found for the 3 types of ointment mentioned above were 0·13 to 2·13 (as Hg or HgO), 0·72 (as $HgNH_2Cl$) and 0·62 (as HgCl), respectively. The method is suitable for any ointment so long as the active constituent has a sp.gr. higher than that of petroleum spirit, is insoluble in neutral organic solvents, is not combined chemically with the basis of the ointment, and can be assayed accurately in the pure state. J. G.

Distribution of Nicotine in Raw Tobacco. T. B. Andreadis and E. J. Toole. (*Z. Unters. Lebensm.*, 1934, **68**, 431–437.)—The distribution of the nicotine in the leaves of a number of tobaccos from northern Greece (Macedonia and Thrace) has been examined. Increase in the nicotine-content is observed on passing from the middle leaves of the plant to either the lower or the upper leaves. Within any one of these three groups of leaves, a certain parallelism exists between the colour and the nicotine-content of a tobacco of a particular sort derived from a definite locality in any one season, the content increasing with the depth of colour of the leaves. In one and the same leaf, the proportion of nicotine increases from the median vein to the edges and from the base of the leaf to the tip, which is the richest in nicotine. T. H. P.

Biochemical

Comparison of the Pepsin and Rennin Activities of the Gastric Secretion of Different Animals. H. Holter and B. Andersen. (*Compt. rend. Lab. Carlsberg*, 1934, **20**, No. 8, 1–18.)—The pepsin and rennin activities of secretions from the stomachs of a number of mammals have been determined by the methods previously described (*id.*, 1933, **19**, No. 19; *Biochem. Z.*, 1932, **255**, 160; 1933, **262**, 99) and expressed in arbitrarily-defined but comparable units. The ratios (*Q*) of these values showed very small individual variations for each species of animal and were, for calves, 0·13 to 0·21; adult cows, 1·6; children, 2·7; adults, 2·5; puppies, 11·5; adult dogs, 12·5; adult pigs, 0·50; Merck's pepsin, 0·34; crystalline pepsin, 0·84. In the case of calves and dogs they are in agreement with the results of Hammarsten (*Z. physiol. Chem.*, 1910, **68**, 119) when these are expressed similarly. The big difference in *Q* in these two cases may explain differences in opinion as to the identity of pepsin and rennin, since some have been based on experiments with the former and some with the latter. Further evidence was obtained of the difference previously noted between the enzymes from calves and those from other animals, the chymosin component being less stable to acid than the pepsin component in the former case; the rate of destruction of chymosin increases with decrease in *p*H value. The general validity of the hypothesis, that enzymes with a particularly powerful rennin action are typical of the ventricular function of infant mammals, is considered to be disproved by the fact that the stomach-enzymes from human adults and children are very similar, but differ from those from calves. It is concluded that the stomach secretions of infant mammals can be divided into two groups, one of which (typified by the calf) secretes a rennin enzyme (Hammarsten's chymosin) differing from pepsin and separable from it, and decreasing in amount with increasing age. In the other group (*e.g.* human beings and probably dogs) the value Q is similar for infants and adults, and cannot be displaced by chemical attack; chymosin is absent. J. G.

Extraction of Zymoflavine by means of Methylal. L. Genevois and L. Espil. (*Bull. Soc. Chim.*, 1934, **1**, 1498–1502.)—The zymoflavine extracted from yeast autolysate by Warburg and Christian (*Biochem. Z.*, 1932, **254**, 348; 1933, **257**, 492 and **266**, 377) may be more easily obtained as follows: 500 g. of fresh bakers' yeast, cold if possible, are shaken with 1 l. of distilled methylal (see p. 113) for 30 minutes, and the clear solvent is afterwards separated and distilled. The aqueous residue in the distilling flask amounts to about 100 ml. and contains the lipids in suspension. The lipids may be obtained by extracting this residue with ether and distilling the ethereal extract; the yield is several grms. per kg. of dry yeast. The residual pasty yeast, saturated with methylal, is left in contact for 30 to 60 minutes, with occasional shaking, with 1 l. of water saturated with methylal, which gives a single phase. After filtration, the methylal is distilled from the yellow filtrate in a vacuum at 30° C. As the flavine is affected on prolonged contact with methylal, this distillation is best carried out on 100- or 200-ml. portions of the filtrate as obtained. The turbid undistilled residue is fermented with fresh yeast (1 g. per 100 ml.) for at least 15 hours at room temperature to remove the sugars. The liquid is then freed from carbon dioxide by a current of air and shaken and left in contact for at least 30 minutes with about 3 per cent. of precipitated chalk. Filtration by suction then yields a clear, lemon-yellow or faintly orange liquid showing green fluorescence in ordinary light and pronounced white fluorescence in ultra-violet rays (Wood's lamp), and remaining unchanged for some weeks in a dark ice-chest. It still contains appreciable amounts of impurities, which may partly be precipitated by neutral lead acetate, but not, as Warburg stated, by the basic acetate. All the chemical properties of the flavines are shown by the solution, and the fluorescence is not affected by blocking the aminic functions with either formaldehyde or a bromoacetate or by oxidising the SH-groups with iodine in faintly acid solution.

The single extraction described above suffices to remove almost all the flavine from the yeast and serves to indicate the flavine-content, which appears to be of the order of a gram per kg. of dry yeast. Brewery yeasts, which multiply almost in absence of oxygen, are much poorer in flavine than bakers' yeast.

T. H. P.

Association of Fat-soluble Vitamins and Anti-oxidants in Plant Tissues. E. M. Bradway and H. A. Mattill. (*J. Amer. Chem. Soc.*, 1934, **56**, 2405–2408.)—It has been shown earlier that vitamin *A* or carotene, and especially vitamin *E* as it exists in foods, are easily destroyed by oxidation in the presence of auto-oxidisable substances, and that their survival in such association depends, partly at least, on the protective action of naturally-occurring or added inhibitors. The presence of anti-oxidants in some vegetable oils and the isolation from lettuce of an anti-oxidant distinct from the vitamins and sterols suggest that such inhibitors may be the protective agencies of the labile fat-soluble vitamins in all plant tissues. Experiment now shows that the fat-soluble vitamins in tomatoes, carrots and wheat-germ oil are accompanied by inhibitors which prolong the induction period of auto-oxidisable fats. After the carotenoid pigments and sterols are largely removed from the unsaponifiable material, diphase distribution between 92 per cent. methyl alcohol and petroleum spirit separates the inhibitors from vitamin *E* in the case of tomatoes and carrots, but with wheat-germ oil both the inhibitor and the vitamin *E* are preferentially soluble in the petroleum spirit. From this observation and from the differing distillation ranges under diminished pressures it appears that the inhibitors in these three materials and in lettuce are all different. Similar evidence indicates the identity of the vitamin *E* derived from different sources. Only small amounts of this vitamin occur in carrots. Lycopene is not active as either vitamin *A* or *E*, but, like carotene, it is pro-oxygenic and shortens the induction period of auto-oxidisable fats. It seems likely that the inhibitors occurring in plants are not confined either to the unsaponifiable fraction of the plant lipids or to the aglucone portion of the glucosides. T. H. P.

Vitamin-*A* Content of the Herring. A. Scheunert and M. Schieblich. (*Z. Unters. Lebensm.*, 1934, **68**, 409–411.)—Rat nutrition experiments with Norwegian and Lerwick herrings show that sexually-mature herrings, whether fresh or smoked, contain vitamin *A* in their genital tissue, the roe being richer in this respect than the male gonads. T. H. P.

Biological and Titrimetric Determination of Vitamin *C*. H. Lund, B. Spur and L. S. Fridericia. (*Biochem. J.*, 1934, **28**, 1825–1828.)—The authors found that, on a vitamin-*C* free diet, guinea-pigs required about 0·7 mg. of ascorbic acid per day. Two samples of lemon juice contained 0·4 and 0·55 mg. per ml., respectively, and dried hips contained about 1·5 per cent. of ascorbic acid. A comparison of these results with those obtained titrimetrically by the use of 2:6-dichlorophenolindophenol shows fairly good agreement; only with the dried hips did the biological method show a higher content, and this was probably due to the incomplete extraction of ascorbic acid by the titration solution. Notice is drawn to the variations in the vitamin-*C* content of lemon juice. S. G. S.

Bacteriological

Preservation of Stock Cultures of Micro-Organisms. A. C. Thaysen. (*J. Inst. Brewing*, 1934, **40**, 469–471.)—The author has found (ANALYST, 1924, **49**, 446) that (*a*) addition of calcium carbonate to a culture of a non-sporing bacterium in vigorous growth, or (*b*) drying a suspension of bacterial spores on clean sterile sand, preserves the viability of such cells or spores for at least 12 months. Results of viability trials on these original cultures are now reported.

B. phosphorescens, B. Kützingianum, the *Saccharomyces* species, *red torula, Penicillium glaucum* and *Aspergillus glaucus* had died, although they were alive at the end of the first 12 months' trial. *B. volutans* and *B. fluorescens liquefaciens* survived for about 2 years, and *Streptococcus haemolyticus* died after 2 weeks. *B. coli com. mesentericus fuscus, subtilis, amylobacter, acetoethylicus* and *paratyphi,* grass coli, *Streptococcus acidi lactici* and *Rhizopus japonicus* had survived for 12 years. The salient morphological and biochemical characteristics before and after the period of preservation are tabulated. J. G.

Water

Rapid Determination of Free Chlorine in Water. L. Leroux. (*Compt. rend.*, 1934, **199**, 1225–1227.)—For the determination of amounts of chlorine below 0·5 mg. per l., *e.g.* in drinking and swimming-bath water, the author proposes an application of the Denigès-Chelle reaction (*id.*, 1912, **155**, 1010), in which a violet colour is given by bromine and an aqueous sulphuric acid solution of magenta (fuchsin). *Reagent.*—Ten ml. of fuchsin solution (0·1 per cent. in water) are mixed with 100 ml. of sulphuric acid (5 per cent.). The mixture becomes colourless in 1 hour and is stable. *Method.*—To 50 ml. of the water contained in a Nessler glass is added a crystal of potassium bromide, and, when it is dissolved, 1 ml. of the reagent and 1 ml. of acetic acid are added. The violet colour produced reaches its maximum intensity in 15 minutes and is stable. The colour may be compared with that produced by a standard solution of chlorine. Since the colour is identical with that of very dilute potassium permanganate, it is suggested that for "field-tests" the colour may be matched by adding drops of *N*/500 permanganate to pure water contained in a Nessler glass of similar size, the amounts of permanganate required to match the colours developed by different amounts of chlorine having been determined in separate tests. The presence of organic matter such as urea (300 mg. per l.) and of nitrates (300 to 400 mg. of nitrogen per l.) was found to be without effect. S. G. C.

Organic

Use of Methylal as a Solvent in Analysis. L. Espil. (*Bull. Soc. Chim.*, 1934, 1, 1502–1503.)—Methylal, $CH_2(OCH_3)_2$, is now prepared industrially, and the commercial product is contaminated only with a small proportion of methyl formate which, however, undergoes gradual hydrolysis at the ordinary temperature, and thus renders the liquid increasingly acid. The formate may be removed by leaving the methylal for some hours in contact with 0·4 per cent. of its weight of a mixture of potassium hydroxide and carbonate and subsequently distilling it. The distillate (b.p. 42° C.) is quite free from acid and, as a solvent, has two advantages over ether: (1) It is more readily soluble in water; at the ordinary temperature, 1 l. of water and 600 ml. of methylal form a homogeneous mixture, and 1 l. of methylal dissolves in 50 ml. of water. (2) It dissolves considerable proportions of many organic acids, but only traces, at most, of mineral acids. Thus, *e.g.* it serves to extract tartaric and malic acids from wines. For a number of organic acids the distribution coefficients [C_p = (concentration of the acid in water) ÷ (concentration of the acid in methylal)] have been determined by shaking 20 ml. of a solution of the acid with 0·2 ml. of concentrated sulphuric acid and 80 ml. of methylal. The values of C_p obtained are as follows, the corresponding values for ether being given in brackets:—Lactic acid, 2·5 (11); succinic, 2·4 (6); citric, 10 (155); malic, 8·6 (71); tartaric, 14 (260). When sodium sulphate is added in order to lower the solubility of the methylal in water, still lower values of C_p are obtained.

Note by Abstractor.—Methylal is stated to have pronounced anaesthetic properties. T. H. P.

Colorimetric Test for Compounds containing CH, CH_2 and CH_3 Groupings contiguous to Negative Groups. M. Goswami, A. Shaha and B. Mukerjee. (*J. Indian Chem. Soc.*, 1934, **11**, 773–775.)—If 2 drops of approx. 2 *N* sodium hydroxide solution are added to 1 ml. of a 0·05 per cent. alcoholic solution of picric acid with subsequent addition of a small quantity of the substance under examination, a red colour results if the substance contains contiguous CH, CH_2 or CH_3 groupings in proximity to the negative groups CHO or CO; thus nitromethane, malonic ester, cyanoacetic ester, acrolein, benzylacetone all give a red colour. This picric acid reaction is general under the conditions described above, whereas Bitto's reagents (*Annalen*, 1892, **269**, 377) fail in many cases. D. G. H.

Comparison of the Susceptibilities of Oils and Fats to Oxidation. C. H. Lea. (*J. Soc. Chem. Ind.*, 1934, **53**, 388–391T.)—The fat is dispersed on filter papers so that a very large ratio of surface to weight is obtained. The filter papers, which are 5·5 cm. in diameter and are fitted with loops of cotton, are weighed, immersed in the oil, pressed between sheets of filter paper to remove excess of fat, weighed again, and rapidly transferred to the jars. The papers are suspended in the jars (2-lb. preserve jars with loosely-fitting lids, to the undersides of which glass hooks are attached), a number of which, complete with lids, have been allowed to reach the temperature of a large electric oven (100° C.). At suitable intervals of time a jar is removed from the oven, and the paper is transferred to a Pyrex test-tube; powdered potassium iodide and a mixture of glacial acetic acid and chloroform (20 ml.) are added, and the peroxide-content is determined. Temperature control is important. Typical curves are given for cod-liver oil, lard, leaf-lard, olive oil, cottonseed oil, beef brisket-fat, beef kidney-fat, butter-fat, castor oil, egg-oil and a vegetable cooking-fat. With beef brisket-fat the initial increase in peroxide-oxygen appears to be arrested for about an hour before rapid absorption sets in, and the same thing is observed, though less definitely, with cottonseed oil. The curve for egg-oil is unusual, in that the peroxide value, after increasing normally for about 4 hours, ceased to rise, and remained constant for the next 20 hours. Possibly the breaks in the curves are due to the action of anti-oxidants. D. G. H.

Anti-oxidants and the Auto-oxidation of Fats, II. H. S. Olcott. (*J. Amer. Chem. Soc.*, 1934, **56**, 2492–2493; *cf.* Mattill, ANALYST, 1931, **56**, 200.)—Forty compounds of various types have been examined with regard to their ability to retard the auto-oxidation at 75° C. of lard, either alone or mixed with cod-liver oil. Only two of the compounds, *viz.* hydroxyhydroquinone and apionol (1:2:3:4-tetrahydroxybenzene) showed anti-oxidant activity comparable in degree with that of the simple polyphenols, pyrogallol, hydroquinone and catechol. The fact that hexahydroxybenzene, although very easily oxidised, has no anti-oxygenic action, emphasises the absence of any simple relation between reducing action and anti-oxidant activity, which seems to depend in some way on a lack of balance in the benzene molecule. Esterification of one or both hydroxyl groups of hydroquinone destroys its action, and the only ester found not completely inactive was pyrogallol monocarbonate. Alkylation proved not quite as destructive as esterification. Mattill's conclusion, that both hydroxyl groups must be bound to the benzene nucleus (*loc. cit.*), is borne out by the inactivity of saligenin, and that of *cis*-1:4-cyclohexandiol emphasises the important rôle of the aromatic ring in anti-oxidants. The quinones were much less active than the corresponding quinols, and maleic, tartaric, and citric acids showed no anti-oxygenic action.

T. H. P.

Chemistry of Arachidonic Acid and its Quantitative Determination. W. C. Ault and J. B. Brown. (*J. Biol. Chem.*, 1934, **107**, 615–622.)—Arachidonic acid $C_{20}H_{32}O_2$ is usually determined by adding bromine to an ethereal solution of a mixture of fatty acids or their esters, and weighing the precipitated octabromides. The arachidonic acid is then calculated by means of the formula:

$$\text{Per cent. of arachidonic acid} = \frac{(\text{polybromide number of mixed acids}) \times 100}{80{\cdot}4}.$$

This is open to suspicion on the ground that the acid prepared by the reduction of the octabromide is not the same as that in the natural fat, and also that linolenic and other highly-unsaturated acids are determined by the same method. It is suggested that the polybromide number of the methyl esters should be used, as the esters prepared by three different methods have been found to give polybromide numbers differing but slightly from each other. Methyl arachidonate may be prepared by fractionation of the methyl esters of suprarenal phosphatide fatty acids, by the lithium soap and acetone method, or by the reduction of methyl octabromo-arachidate. In the lithium soap and acetone method 100 g. of fatty acids are weighed into a 3000–ml. flask and dissolved in 400 ml. of anhydrous acetone. This solution is titrated with aqueous 5 *N* lithium hydroxide solution until neutral to phenolphthalein, and enough water is added to make the total aqueous solution up to 120 ml. To this solution 1500 ml. of anhydrous acetone are added, with stirring, and the flask is kept in ice for 4 hours. The insoluble soaps are then filtered off and washed twice with 90 per cent. acetone. The soluble soaps are decomposed with dilute hydrochloric acid, about half the acetone is removed by distillation, and the remaining solution is diluted with several volumes of water and finally extracted with ether. The extracted fatty acids are esterified with methyl alcohol, and the methyl esters are distilled under reduced pressure. If the reduction method of preparation is used, 1 kg. of the freshly-distilled methyl esters of the fatty acids is dissolved in 4 l. of dry ether and brominated at 0° C. with constant stirring, and the precipitated bromides are washed seven times by decantation with cold ether. One hundred g. of the precipitate are then suspended in 1 l. of methyl alcohol and boiled with 100 g. of zinc dust and 1 to 2 ml. of concentrated hydrochloric acid under a reflux condenser for 6 hours. About one-half of the alcohol is then boiled off and the residue is centrifuged. The clear alcoholic solution is poured into water and acidified to decompose any zinc arachidonate. The methyl ester is then extracted with ether and separated. The ether is distilled from the ethereal layer, and the residue is again boiled under reflux with methyl alcohol containing dry hydrochloric acid gas. Finally, the solution is distilled under reduced pressure. The following table gives a summary of the analytical figures obtained on the esters prepared by the different methods:

Method of preparation	Mean mol. wt. (ester)	Iodine value	Approx. purity Per Cent.	Poly-bromide number	Polybromide number based on 100 per cent. purity
Fractionation three times ..	311·5	261·8	85	74·4	87·6
Lithium soap and acetone method on whole acids	319·2	286·2	90	76·2	84·7
Same followed by fractionation ..	318·5	304·5	95	81·0	85·2
Reduction of bromides	317·8	316·9	100	86·5	86·5
Reduction of bromides	317·8	315·4	100	84·3	84·3
Theory, methyl arachidonate ..	318·0	319·0	—	—	—

The formula suggested for calculating arachidonic acid is

$$\text{Per cent. of methyl arachidonate} = \frac{(\text{polybromide number of mixed methyl esters}) \times 100}{86{\cdot}5},$$

but the polybromide number of the acid or acids present must be known or determined before using the formula. S. G. S.

Linaloe Oil, Mexican and Indian. W. H. Simmons. (*Perf. and Essential Oil Record*, 1934, **25**, 378–379.)—True linaloe oil is distilled from the wood of various species of the *Burseraceae*, but oil of inferior odour, distilled from the seeds and fruits of the trees, is also met with, sometimes in admixture with the wood oil. Until about 1910 Mexican dextro-rotatory linaloe oils were rare, and the average ester-content was some 10 per cent., but from 1911 onwards the ester-content has shown a marked increase, until at the present time even 25 to 30 per cent. of esters may be found. Similarly, dextro-rotatory oils occur more frequently than in former years. During the last few years very fragrant Indian linaloe oils, grown from Mexican seed, have come on the market. The Indian wood and seed oils are very similar, but their sp.gr. is higher, on the average, than for the Mexican oils; the optical rotation is almost invariably positive (between 0 and +2°); the refractive index is lower than with Mexican oils, and the ester-content is high, lying generally between 35 and 44 per cent., as linalyl acetate. The limits for the analytical constants of (*a*) 7 samples of Indian linaloe wood oil and (*b*) 6 samples of seed oils were:—Sp.gr. at 15° C. (*a*) 0·8887 to 0·8981; (*b*) 0·8878 to 0·8911; $[\alpha]$, (*a*) +1°0′ to +2°30′; (*b*) 0°18′ to +2°18′; $n_D^{25°}$, (*a*) 1·4612 to 1·4628, (*b*) 1·4600 to

1·4623; ester (as linalyl acetate), (*a*) 37·3 to 44·9 per cent.; (*b*) 31·5 to 44·1 per cent.; alcohols (as linalool), (*a*) 73·3 to 76·1, (*b*) 71·8 to 74·7 per cent.; solubility in 70 per cent. alcohol, (*a*) 1 in 1·5 to 1 in 2, (*b*) 1 in 2 to 1 in 2·5. D. G. H.

Action of Hot Concentrated Sulphuric Acid on Dyes. R. B. Forster. (*J. Soc. Chem. Ind.*, 1934, **53**, 384T.)—The separation of the various classes of dyes may be facilitated by a study of their behaviour with hot concentrated sulphuric acid. The classes behave in a more or less characteristic way, except that the indigoid and anthracene dyes give specific, rather than general, reactions. A very small quantity of dye is dissolved in cold concentrated sulphuric acid, the colour observed, and the temperature then gradually raised to the b.p.

ACTION OF CONCENTRATED SULPHURIC ACID ON DYES

Class of dye	Colour in cold conc. sulphuric acid	Reaction on heating
Nitroso	Golden-orange	Decolorised→ pale straw-colour on boiling
Azo	Yellow to green	Decolorised→ carbonises
Stilbene-azo	Magenta to bluish-red	Decolorised, very little carbonisation on boiling
Stilbene	Yellowish-red to blue	Decolorised, practically no carbonisation on boiling
Thiazole	Pale yellow to brownish-yellow	Slightly darker, carbonises only after prolonged boiling
Triphenylmethane*	Yellow to yellowish-red	Darker, carbonises very easily
Diphenylmethane	Colourless	Reddish, carbonises rapidly
Xanthene	Yellow to brownish-red	Redder→ paler→ carbonises on boiling
Oxazine	Red to blue	Darker→ carbonises
Azine	Green	Discharges and carbonises
Induline	Blue	Slightly paler, then carbonises
Thiazine	Green	Darkens→ carbonises
Quinoline	Yellow	Slightly paler, very little change even on prolonged boiling
Acridine	Pale yellow (fluorescent)	Slightly darker (fluorescence disappears), carbonises only with difficulty

* Sulphonated triphenylmethane dyes give a redder shade and are more resistant to carbonisation.

D. G. H.

Analysis of Asphalt, Bitumen and Tar Materials used in Road Construction. D. M. Wilson. (*J. Soc. Chem. Ind.*, 1934, **53**, 924–929.)—An account is given of the occurrence, manufacture, and uses of asphalt, tar, etc., in road construction, and data on the properties of the materials are collected in tabular form. Some notes are added on methods of analysis in amplification of the standard methods. *Bitumen-content.*—Bitumen is determined by difference on extracting the bitumen in carbon disulphide. Non-inflammable solvents such as trichloroethylene or perchloroethylene may be employed, but filtration is slower than with carbon disulphide. Loss of fine particles by "creeping" during filtration of the extract may be avoided by sealing the funnel with a glass plate. With steam-rolled asphalt, which may contain up to 45 per cent. of 1-in. stone chippings, it is necessary to dissolve the bitumen from at least 3 kg. of the sample in order to obtain representative results. The "penetration value" of the bitumen recovered by evaporation of the solvent should be determined, as it shows whether the material has been overheated in course of manufacture. *Tarmacadam.*—Suitable apparatus, in which the tar may be extracted in naphtha and any water present in the aggregate may be collected at the same time in a modified Dean and Stark tube, has been described (*Highways and Bridges*, 1934, 1, Pt. 5, 11). The residual slag should be analysed for silica and lime-content. It has been found that if the ratio CaO : SiO_2 exceeds 1·4, the slag is liable to crumble. *Identification of natural asphalt rock.*—Natural asphalt, which is a limestone naturally impregnated with bitumen, is often adulterated with limestone in order to cheapen the material. On examination of the mineral aggregate, after removal of the bitumen, under ultra-violet light, the natural asphalt rock usually shows a light brownish fluorescence, whilst crystalline limestones show a dark brown colour; there are exceptions. Examination of the aggregate with a binocular microscope is also helpful, especially if the unknown material is compared with known rocks. The natural rock is usually porous and often contains fossils, whilst added limestone is generally crystalline. The aggregate may be dissolved, as far as possible, in cold hydrochloric acid, and the residue may be examined by separation methods involving the use of heavy liquids, *e.g.* bromoform. Some limestones yield a residue containing fluorite (heavy) and chert (light), which are not present in the more commonly used asphalt rocks. *Identification of Trinidad Epuré.*—The heavy minerals which can be separated from the mineral aggregate of Trinidad Epuré by means of bromoform include titanite, zircon, rutile and glaucophane; glaucophane, whilst usually present in small amount, is blue in colour, and is characteristic of Trinidad asphalt. *Identification of bitumens by colour value*: Bitumen may be identified by examination of the colour of a dilute solution in perchloroethylene (0·25 g. in 100 ml.) contained in a glass cell, 0·5 cm. wide; a Lovibond tintometer is employed.

CHARACTERISTICS OF BITUMENS

	Penetration at 25° C.	Colour value		
		Neutral tint	Orange	Yellow
(*a*) *Bitumen recovered from asphalt rocks* :				
St. Jean	79	1·4	6·3	32·3
Sicilian	76	2·4	7·1	40·5
Val de Travers	73	2·0	8·5	49·5
(*b*) *Bitumen recovered from Trinidad Epuré and its mixtures* :				
Trinidad Epuré	11	2·1	6·9	11·1
75 per cent. Trinidad Epuré 25 per cent. Texaco Flux	71	1·1	6·1	35·8
50 per cent. Trinidad Epuré 50 per cent. Venezuelan 45	36	4·5	11·0	44·5
50 per cent. Trinidad Epuré 50 per cent. Panuco 45	36	2·6	9·7	47·7
(*c*) *Asphaltic Bitumen* :				
Panuco	45	3·3	11·0	45·7
Light Mexican	40	7·2	12·8	49·0
Venezuelan	42	7·1	12·9	40·0

S. G. C.

Inorganic

Preparation, Storage and Use of Standard Carbonate-free Sodium Hydroxide Solutions. W. W. Kay and H. L. Sheehan. (*Biochem. J.*, 1934, **28**, 1795–1797.)—Solutions of sodium hydroxide which are carbonate-free down to dilutions of $N/100$ may be prepared by the interaction of solutions of barium hydroxide and sodium sulphate. The sodium sulphate solution is freed from carbonates by making it slightly acid and boiling, and excess of this solution is used, as the presence of sodium sulphate has no effect on titration. A description is given of a new arrangement for storing and using such a solution under conditions of minimum carbonate contamination. S. G. S.

Determination of Sulphur in Cast Iron. E. W. Colbeck, S. W. Craven and W. Murray. (*Foundry Trade J.*, 1934, **51**, 308–310.)—Methods depending on the evolution of sulphur compounds by acid have been found to be inaccurate when applied to cast iron, and with the wet oxidation method it was difficult to secure satisfactory results. An improved method is proposed, in which the finely-ground sample is acted upon by copper ammonium chloride solution, which rapidly dissolves out the iron and leaves the sulphur in the carbonaceous residue, from which the sulphur can then be readily extracted by bromine and hydrochloric acid, giving a solution in which the acid concentration may be suitably adjusted for the precipitation of barium sulphate. *Method.*—A 4-g. sample (passing 22-mesh B.S.S. sieve) is weighed out into a 350-ml. conical flask fitted with a ground-in glass stopper or with a rubber bung which has been previously boiled in successive portions of hydrochloric acid until the acid gives no reaction for sulphate or sulphide; 250 ml. of copper ammonium chloride solution (30 per cent. in water acidified with 5 per cent. of concentrated hydrochloric acid) are added, and the flask is stoppered and shaken. The insoluble residue is filtered off on a pulp filter and washed until free from iron salts with a solution consisting of 1 vol. of copper ammonium chloride solution with 5 vols. of water, and finally with water. The residue is extracted with a mixture of 50 ml. of water, 2 ml. of bromine, and 5 ml. of concentrated hydrochloric acid by heating on a water-bath for half an hour. Bromine is then boiled off and the liquid is filtered, the washing being done with cold water. The filtrate is diluted to 200 ml. and heated to boiling, and 10 ml. of 10 per cent. barium chloride solution are added. The precipitate is allowed to settle overnight, filtered off, washed with cold water and ignited. The cited results of tests on various samples of grey and white cast iron, obtained by this and other methods, are held to confirm the validity of the present method.
S. G. C.

New Method for the Determination of Small Quantities of Aluminium. Application to Vegetable Substances. P. Meunier. (*Compt. rend.*, 1934, **199**, 1250–1252.)—Photometric determination of the turbidity formed by cupferron with small amounts of aluminium in a solution of regulated *p*H value is proposed. Iron, copper, titanium, etc., which also give precipitates with cupferron, can be removed by previous precipitation with cupferron in more strongly acid solution, the precipitate being separated by extraction with chloroform. *Method.*—The ash from 0·5 to 1·0 g. of the dry vegetable substance is dissolved in about 10 ml. of 0·6 *N* hydrochloric acid. The solution is filtered and a 5 per cent. solution of cupferron is added until the presence of an excess is shown by the formation of a whitish precipitate. The liquid is extracted by shaking with two successive portions of chloroform. To the clear aqueous solution, transferred to a 50-ml. graduated flask, 5 ml. of 20 per cent. ammonium acetate solution and 0·5 ml. of the cupferron solution are added, and the liquid is diluted to 50 ml. The flask is shaken for a few seconds. After 20 minutes, and again after 30 minutes, the opacity of the turbidity is measured by means of a Féry spectrophotometer or a photo-electric nephelometer. Aluminium solutions of known strength are employed as standards, and are treated in a similar manner. In test experiments, amounts of aluminium from 0·01 to 0·06 mg., added to 1 g. of vegetable matter, were recovered with an accuracy of 5 per cent. Other results obtained by this method have been confirmed by the gravimetric method of Bertrand and Levy (*Compt. rend.*, 1931, **192**, 525). S. G. C.

Precipitation of Aluminium by means of *o*-Hydroxyquinoline in presence of Iron, Nickel, Cobalt, Copper, Chromium, and Molybdenum. T. Heczko. (*Chem.-Ztg.*, 1934, **58**, 1032–1033.)—The method involves the conversion of the iron, nickel, etc., into complex cyanides, in which form they are not precipitated by *o*-hydroxyquinoline. *Method.*—To the solution of the alloy (0·5 to 1 g.) in *aqua regia* are added 8 to 10 g. of dissolved tartaric acid; it is diluted to 100 ml. and rendered ammoniacal; 5 to 10 g. of potassium cyanide are added, and hydrogen sulphide is bubbled in for 10 minutes in order to reduce iron to the ferrous condition, when it becomes converted into ferrocyanide. After 1 hour any precipitate of manganese sulphide, silica, etc., is filtered off. [Manganese sulphide is difficultly filterable, so that if appreciable amounts of manganese are present (more than 5 mg.), it is desirable to filter off an aliquot portion, re-filtering, if necessary, to obtain a clear solution. If much silica is present, some alumina is likely to be adsorbed on it, and it is therefore necessary to treat it as follows:—It is ignited in a platinum crucible; hydrofluoric acid and sulphuric acid are added, and the liquid is evaporated to dryness; the residue is fused with potassium bisulphate and dissolved in dilute sulphuric acid; a few g. of ammonium sulphate and a few drops of hydrogen peroxide are added, and the aluminium and any iron are precipitated with ammonia, methyl orange being used as indicator; the precipitate is filtered off, washed, and dissolved in dilute sulphuric acid; some tartaric acid is added, the solution is rendered ammoniacal and added to the main filtrate.] The filtrate is heated to boiling and a slight excess of a concentrated solution of *o*-hydroxyquinoline in alcohol is slowly added, with stirring. After 2 minutes the precipitate is filtered off on a sintered glass crucible, washed with warm water, and dried at 150° C. The weight of the precipitate, multiplied by 0·0587, gives the weight of aluminium present. *Modification for chromium alloys.*—As a very considerable quantity of tartaric acid is required to maintain tervalent chromium in solution, it is desirable to convert the chromium into chromate, as follows:—To the solution of the alloy in dilute sulphuric acid are added a few g. of ammonium persulphate and a few mg. of silver nitrate, and the solution is warmed. When oxidation is complete and any manganese has been converted into permanganic acid, a few ml. of hydrochloric acid are added, and the solution is boiled and subsequently cooled. This solution is then treated as for non-chromium alloys. S. G. C.

Detection of Chlorine and Bromine in Gases or Solutions by Means of Resorufin. H. Eichler. (*Z. anal. Chem.*, 1934, **99**, 272–275.)—The solution of resorufin in alkali carbonate, of red colour with intense yellow-red fluorescence, yields with bromine tetrabromoresorufin, the alkali salts of which are blue; chlorine acts like bromine. For the detection of either, the solution containing sodium carbonate or bicarbonate, but not hydroxide or free acid, is treated with a minimum of reagent (0·1 g. of resorufin and 1·5 g. of sodium carbonate in 100 ml. of water). Substitution takes place almost instantly in the cold, a blue colour being obtained. An excess of reagent produces a yellow-red fluorescence; a large excess of halogen destroys the blue reaction product. For the detection of the halogens in air, etc., the gas is led through a dilute solution of the reagent; chlorine and bromine destroy the fluorescence. W. R. S.

Detection of Hydrosulphite and Nascent Hydrogen by Means of Resazurin. H. Eichler. (*Z. anal. Chem.*, 1934, **99**, 270–272.)—The reagent is a solution of 0·1 g. of resazurin or its sodium salt and 0·3 g. of sodium carbonate in 100 ml. of air-free water. The solution to be tested, which must contain free sodium carbonate, is treated with a minimum of reagent. If no hydrosulphite ($Na_2S_2O_4$) is present, the blue colour of the reagent and its brown fluorescence remain unaltered; otherwise, the colour is discharged in the cold. Further addition of reagent will then produce a red fluorescence, due to the conversion of the hydroresorufin into resorufin. Sulphites react sluggishly; thiosulphates do not reduce. Ferrous or stannous hydroxide reduces in the cold. In acid solution, thiosulphates or sulphites reduce the reagent acidified with sulphuric acid, as also do metals by producing nascent hydrogen. Stannous or titanous salts likewise decolorise the reagent; hydrochloric acid should not be present, as it forms chloro derivatives at higher temperatures. W. R. S.

Analysis of Reducing Sulphur Acids. E. Cherbuliez and H. Herzenstein. (*Helv. Chim. Acta*, 1934, **17**, 1582–1587.)—*Determination of Hydrogen Sulphide.*—To the approximately neutral solution is added a suspension of precipitated cadmium carbonate, and the whole is shaken for half a minute, when the hydrogen sulphide reacts to form cadmium sulphide. The precipitate is filtered off, washed with water, and then stirred up with a little water and a slight excess of 0·01 *N* iodine solution. The excess of iodine is titrated with standard thiosulphate solution, starch being used as indicator. Hydrogen sulphide may thus be separated from sulphurous, thiosulphuric, and hydrosulphurous acids, which do not react with cadmium carbonate. *Determination of Thiosulphuric Acid.*—The reaction between sodium azide and iodine according to the equation $2NaN_3 + 2I = 3N_2 + 2NaI$ is catalysed by thiosulphuric acid, and the extent of the reaction is proportional to the amount of thiosulphuric acid present; the thiosulphuric acid becomes simultaneously oxidised to tetrathionate. The following method is proposed:—To 5 ml. of the solution [? neutral: *Abstractor*] are added 0·2 g. of sodium azide and a few drops of starch solution. Standard iodine solution (0·01 *N*) is added, drop by drop, with constant stirring, until the starch-blue persists for half a minute. The thiosulphate value of the iodine solution is determined by titrating a standard thiosulphate solution under similar conditions. Hydrogen sulphide, hydrosulphurous acid, and thiocyanic acid interfere. *Reactions of Thiosulphuric Acid in Dilute Solutions.*—(*a*) The lower limit for the detection of thiosulphates by acidifying and observing the turbidity of sulphur produced is about 0·001 *N*. (*b*) At *p*H 6 thiosulphuric acid is stable, and colloidal sulphur produced, *e.g.* by the action of iodine on hydrogen sulphide, dissolves readily in sulphurous acid, yielding thiosulphuric acid. *Detection of Sulphurous Acid.*—Sulphurous acid bleaches magenta (fuchsin), and when formaldehyde is subsequently added, the colour re-appears (Votoček, *Ber.*, 1907, **40**, 414); this reaction has been found sufficiently sensitive to detect 2 ml. of 0·01 *N* bisulphite solution per l. S. G. C.

Measurement of Atmospheric Sulphur Pollution by means of Lead Peroxide. B. H. Wilsdon and F. J. McConnell. (*J. Soc. Chem. Ind.*, 1934, **53**, 385–388T.)—The method for measuring pollution of the atmosphere due to the burning of coal, devised for the Atmospheric Pollution Research Committee of the Department of Scientific and Industrial Research, has now been in use for three years, and its general adoption has been recommended to co-operating local authorities. It consists in the determination of the sulphur dioxide present after absorption of the sulphur compound on a prepared surface of lead peroxide (ANALYST, 1933, **58**, 284). The lead peroxide is mixed with a 1 per cent. mucilage of gum tragacanth, which produces the required matt surface without reduction of porosity, and the resulting paste is applied to a cloth surface wrapped round a porcelain former. The ranges of proportionality between the rate of absorption and the concentration of sulphur dioxide and period of exposure were investigated, for the particular paste and type of cylinder, by placing cylinders in a small wind tunnel through which was passed a stream of air containing known quantities of sulphur dioxide, and it was evident that within the limits of experimental error the rate of absorption remains approximately linear, even when as much as 15 per cent. of the absorbent has been converted. Since wind velocity, as well as temperature, may have an effect and the method is for outdoor exposure, it is particularly important to establish a statistical relation by which the range of variation in the relation between lead peroxide sulphation and the volume concentration of sulphur dioxide may be assessed, rather than to rely on results obtained under artificial conditions. For small velocities the rate of absorption was found to vary inversely as the fourth root of the air velocities, and these variations, together with those due to temperature, have been estimated and compared with the range of variation calculated statistically from two years' observations, in the course of which both the volumetric and lead peroxide methods were used. The observed variation is greater than that attributable to wind and temperature, and is probably dependent on errors in the volumetric method and on differences in the exposure at the points of observation. The lead peroxide method provides a simple way of estimating prevalent concentrations of sulphur dioxide if exposures are so made that corrections may be applied for effects of wind velocity and temperature. D. G. H.

Microchemical

Apparatus and Methods for Micro-sublimation. R. Fischer. (*Mikrochem.*, **1934**, **15**, 247–271.)—Various apparatus and methods for micro-sublimation are described, and, in particular, the author's improved model of the electrically-heated combined m.p. and sublimation block, which is provided with means for accurate temperature measurement, an automatic temperature regulator, and glass covers for sublimation under reduced pressure.

J. W. M.

Collected References. Electrographic Methods. R. Jirkovský. (*Mikrochem.*, 1934, **15**, 331–343.)—A summary of the methods, as used by different authors, and their applications, are described. The applications are mainly concerned with the examination of metals and alloys, when a metal plate is used as cathode and the metal under examination as anode (or *vice-versa*), and "spot" paper impregnated with a reagent for the metal going into solution is placed between the anode and cathode. References to 20 papers are given. J. W. M.

Spot Tests for Organic Compounds. III. F. Feigl and V. Anger. (*Mikrochem.*, 1934, **15**, 23–25.)—*Detection of Sulphonic Acids.*—Either a little of the solid substance or a drop of the test solution, evaporated to dryness in a porcelain micro-crucible, is heated with a few drops of thionyl chloride until fumes appear, after which two drops of a saturated alcoholic solution of hydroxylamine hydrochloride and a drop of acetaldehyde are added, and the mixture is rendered alkaline with 5 per cent. sodium hydroxide solution. After a few moments the mixture is acidified with alcoholic hydrochloric acid, and, finally, a drop of a dilute aqueous solution of ferric chloride is added; a brown to violet colour or precipitate indicates that a sulphonate was present.

The reactions that take place are expressed by the following equations:

$$\begin{gathered}
R\mathrm{SO_3H} + \mathrm{SOCl_2} \rightarrow R\mathrm{SO_2Cl} + \mathrm{SO_2} + \mathrm{HCl} \\
R\mathrm{SO_2Cl} + \mathrm{NH_2OH} \rightarrow R\mathrm{SO_2(NHOH)} + \mathrm{HCl} \\
R\mathrm{SO_2(NHOH)} + \mathrm{CH_3CHO} \rightarrow \mathrm{CH_3C{\cdot}(NHOH)} + R\mathrm{SO_2H} \\
3\mathrm{CH_3CO(NHOH)} + \mathrm{FeCl_3} \rightarrow \mathrm{Fe[CH_3CO(NHO)]_3} + 3\mathrm{HCl} \\
3R\mathrm{SO_2H} + \mathrm{FeCl_3} \rightarrow \mathrm{Fe}[R\mathrm{SO_2}]_3 + 3\mathrm{HCl}.
\end{gathered}$$

When a sulphonic acid salt is being tested it should be evaporated with hydrochloric acid before treatment with thionyl chloride. Dyestuffs, the colours of which interfere with the observation of the test, may be decomposed with a few drops of bromine water. Amino-groups, which affect the conversion of the sulphonic acid into the chloride, may be decomposed with sodium nitrite. The *detection limit* is given for the following sulphonic acids:—Benzene chlorosulphonate, 12γ; naphthalene-β-sulphonic acid, 20γ; sulphanilic acid, 25γ; potassium *p*-benzene disulphonic acid, 10γ; "H" acid, 15γ; helianthine, 30γ. The colour-reaction with all these compounds is brown. J. W. M.

Spot Tests for Organic Compounds. IV. F. Feigl, V. Anger and O. Frehden. (*Mikrochem.*, **1934**, **15**, 181–190.)—*Detection of Nitroso Compounds.* The Liebermann reaction (*Ber.*, **1882**, **15**, 1529; **1883**, **16**, 1473; **1887**, **20**, 3231) and the Baudisch reaction (*Ber.*, **1921**, **54**, 413; **1922**, **55**, 2702; **1929**, **62**, 2699, 2706) have been adapted for use on the micro-scale as "spot" tests. For the Liebermann test a crystal of pure phenol and a few granules of the substance under examination are mixed in a micro-crucible and heated to melting. The fused mass is allowed to cool and treated with a few drops of pure sulphuric acid. A dark cherry-red colour is usually produced, changing on dilution and treatment with 4 *N* alkali, generally to blue. For the Baudisch reaction the most suitable prusso-salt to use as reagent is sodium pentacyanammino-ferroate ($Na_3[Fe(CN)_5NH_3]$), used in 1 per cent. solution. This compound is prepared by mixing sodium nitroprusside with three times its amount of concentrated ammonia; the mixture is cooled with ice and, after 24 hours, diluted with alcohol, filtered and washed. For the test, a drop of the solution under examination is mixed with a few drops of the reagent and allowed to stand for the colour to develop. The results obtained with certain nitroso compounds are given in the following table:

	Liebermann reaction		Baudisch reaction	
Compound	Identification limit	Colour change	Identification limit	Colour change
	γ		γ	
p-Nitroso dimethylaniline	0·5	red to yellow-green	0·15	green
p-Nitroso phenol	0·4	red to blue	0·15	dark green
α-Nitroso β-naphthol	0·5	red to blue	1	olive green
β-Nitroso α-naphthol	0·6	red to green	1	olive green
Tetrahydro β-nitroso-α-naphthol	0·5	red to green	—	no reaction
iso-Nitroso acetyl acetone	1	dark red to green-yellow	2·5	brown lilac
iso-Nitroso acetophenone	1	red to yellow	3	green

Detection of nitro compounds.—The Baudisch test, described above, can be used for nitro compounds after reduction to nitroso compounds. A drop of the solution under examination is mixed with a few drops of the reagent and a drop of 4 *N* alkali solution in a micro-crucible, and the test solution is reduced electrolytically, a nickel wire being used as cathode and a lead wire as anode, and the current passed for 10 to 30 minutes. If, on adding alkali before electrolysis, a colour-change occurs, a drop of 5 per cent. sodium thiosulphate solution is used instead of the electrolyte. A blank test should be carried out. The reaction is useful for differentiating different kinds of artificial musks. A table is given of 34 different nitro-compounds with the limit of identification and colour formed in each case. *Detection of organic hydrazine derivatives.*—Many hydrazine derivatives also react with sodium pentacyanammino-ferroate to give coloured products on standing. A table is given showing the colours in neutral and in alkaline solution and the identification limit obtained with 10 hydrazine derivatives. J. W. M.

Detection of Aldehydes and Ketones. II. R. Fischer and A. Moor. (*Mikrochem.*, 1934, **15**, 74–87.)—Further reagents are suggested for the detection of aldehydes and ketones by the formation of crystalline derivatives, and the determination of the m.p. of the derivatives under the microscope (*Mikrochem.*, **1933**, **13**, 123; Abst., ANALYST, **1933**, **58**, 569). The additional reagents are:—(i) *o*- and *m*-nitrophenylhydrazine, used mainly as a saturated solution in 15 per cent., and, sometimes, in 30 per cent. acetic acid; the solution, which should be kept in glass-stoppered bottles, is stable for only 3 or 4 days. (ii) *m*-nitrobenzene hydrazide (m.p. 152° C.) used in saturated solution in 30 per cent. acetic acid.

(iii) Semicarbazide (m.p. 96° C.), used as a saturated aqueous solution, or 2 g. are mixed with 2 g. of sodium acetate and dissolved in 6 g. of water; when the reagent solution becomes cloudy it should be discarded. (iv) Semi-oxamazide (m.p. 234° C.) used either as a saturated aqueous solution or dissolved in 30 per cent. acetic acid. This is a useful reagent, but the derivatives tend to be very volatile in the region of the m.p., which must therefore be determined with rapid heating (4° to 6° C. per minute). (v) Thio-semicarbazide (m.p. 183°–184° C.) is employed somewhat less frequently as a reagent; it is used either as a saturated aqueous solution or dissolved in 20 per cent. potassium acetate solution. Reactions of the following aldehydes and ketones with the reagents are described, and a table is given of the m.p. of the derivatives formed:—Formaldehyde, acetaldehyde, furfural, acrolein, *iso*-valeraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, *p*-chlorobenzaldehyde, cinnamaldehyde, salicylaldehyde, anisaldehyde, piperonal, cuminaldehyde, vanillin, acetone, acetophenone, chloracetophenone, carvone, menthone, thujone, methyl butyl ketone, and ethyl *iso*propyl ketone. J. W. M.

Test for Small Amounts of Fluorine. S. Kühnel Hagen. (*Mikrochem.*, 1934, **15**, 313–315.)—Very small amounts of hydrogen fluoride which are insufficient to etch glass surfaces change its quality slightly, so that sulphuric acid no longer runs over it smoothly, but agglomerates like water on a greasy surface. A small narrow test-tube is thoroughly cleaned with potassium dichromate completely dissolved in 1 to 1·5 ml. of hot concentrated sulphuric acid, which is run over the whole interior surface. A little of the solid substance to be tested for fluorine or a drop of the solution is added, and the mixture is boiled. In the presence of fluorides small or large flecks will be seen above the condensation boundary of the sulphuric acid on the glass from which the acid withdraws. When large amounts of fluorine are present this effect is instantaneous. The detection limit is 0·5γ of fluoride. Other halogens, sulphur compounds, nitrates, phosphates, carbonates, or salts of zirconium, titanium, uranium, or vanadium do not interfere. Iron and molybdenum compounds slightly reduce the sensitivity. Complex radicles such as BO_2' and SiO_3'' reduce the sensitivity to 5γ in the presence of 0·3 per cent. of SiO_3 or 0·5 molar BO_2. J. W. M.

Physical Methods, Apparatus, etc.

Fluorescence Test for Olive Oils. T. T. Cocking and S. K. Crews. (*Quart. J. Pharm.*, 1934, 7, 531–534.)—The sample is treated with decolorising charcoal (B.D.H.) as described (*Pharm. J.*, 1934, **133**, 86; Abst., ANALYST, 1934, **59**, 652), and on the next day the clear supernatant oil is filtered and examined in a thin bottle of non-fluorescent glass in filtered ultra-violet rays (310 to 390$m\mu$). Genuine virgin olive oils, which had originally a deep golden-yellow fluorescence, became almost colourless and showed only a faint and dull blue fluorescence. The usual adulterants which have low Bolton–Williams values (arachis, sesame and tea-seed oils) and "refined" olive oils were all bleached, but retained their original blue fluorescence, which is usually taken as an indication of this form of adulteration. Certain olive oils which have recently appeared on the market have an opaque dark purple or chocolate-coloured fluorescence before treatment, and it is suspected that this is due to the intentional addition of some substance to mask the blue fluorescence of the above adulterants. The charcoal treatment removed this masking fluorescence completely, leaving the blue fluorescence. Virgin olive oils which have been heated at 300° C. also show a blue fluorescence (*cf.* Musher and Willoughby, *Oil and Fat Ind.*, 1929, **6**, 15), which is not removed by charcoal. About 5 per cent. of arachis or tea-seed oil is detectable by the method; intense fluorescence may be recorded by the Lovibond tintometer.

J. G.

Fluorescence and Detection of Rhapontic Rhubarb. T. E. Wallis and E. R. Withell. (*Quart. J. Pharm.*, 1934, 7, 574–580.)—Further details are given of the test previously described (*Pharm. J.*, 1934, **133**, 90; Abst., ANALYST, **1934**, **59**, 652). The prepared strips of cellulose wadding paper, saturated with the alcoholic tinctures of the sample and of genuine Chinese rhubarb and dried for 20 minutes on a sheet of glass in the dark, are examined beneath the ultra-violet lamp as rapidly as possible. The violet fluorescence of rhapontic rhubarb gradually disappears on exposure of the strips to ultra-violet light or to diffused daylight, and is completely replaced in each case by the same pale yellow fluorescence after 20 minutes and 4 days, respectively; the effect is less marked on the unexposed side of the strip, and with powdered rhubarb. The intensity of the fluorescence of the strips is reduced visibly after 30 minutes at 70° C., and to a considerable extent after 18 hours; it is also reduced if the maceration is carried out in daylight. Filter papers used for the strips vary in appearance in ultra-violet light, those containing cotton fibres being blue, whilst wood cellulose does not fluoresce and is preferred for the test.

(*Abstractor's Note.*—The fluorescence of paper fibres depends on the nature of the treatment they have undergone rather than on the origin of the fibres. It also alters when the paper is exposed to ultra-violet light, to daylight, or to heat, and this may influence the changes noted above.)

J. G.

Reviews

HANDBOOK OF CHEMISTRY. By N. A. LANGE, Ph.D. Pp. 1265. With Appendix of Mathematical Tables and Formulas by R. S. BURINGTON, Ph.D. Pp. 248, and Index, pp. 29. Sandusky, Ohio: Handbook Publishers, Inc., 1934.

This book consists chiefly of tables of chemical and physical constants, and it also contains a mass of information which should render it useful as a work of reference in several branches of pure and applied science. Recent investigations, where available, have been laid under contribution, and the work deserves high praise both for what is included and for what is omitted.

The tables of physical constants of inorganic and of organic compounds are very full, occupying 350 pages of fairly close print; the references to "Beilstein," which are given for most of the organic compounds, link the book to the whole field of organic chemistry. The data for fats, oils and waxes, alkaloids, glucosides, and resins are given very fully in separate tables. Electrometric and colorimetric methods for determining *p*H values are described.

In the tables showing the relations between specific gravity, percentage content, hydrometer readings, etc., of aqueous solutions, degrees Baumé are given according to the formula for the American scale. So long as the Baumé hydrometer remains in vogue for industrial purposes, chemists must, perforce, use it. As the author points out, however, there are about 36 Baumé scales in use; the suppression of at least 34 of them by international action is certainly called for.

Considering the scope of the book and the enormous amount of information that it contains, the errors observed are very few. In the brief description of the elements on pp. 20—42, oxides and hydroxides are in some cases included amongst the "salts" formed by the element; on p. 35 "Niton" is misspelt "Nitron," and on p. 512 witherite is stated to be barium sulphate. Helium was isolated in 1895, and not in 1898, as stated on p. 27. Alabamine (eka-iodine), illinium and virginium (eka-caesium) are included amongst the elements, but for alabamine and virginium, at least, the claim to such inclusion can hardly be regarded as established, and the statement under the heading "Alabamine" on p. 20 that "The discovery of this element marks the end of the search for new elements from numbers 1 to 92 . . ." is rather a rash one.

L. EYNON

THE PRACTICE OF ABSORPTION SPECTROPHOTOMETRY. By F. TWYMAN, F.Inst.P., F.R.S., and C. B. ALLSOPP, M.A., Ph.D. Second Edition. Pp. 144, 45 Figs. London: Adam Hilger, Ltd. Price 12s. 6d. net.

The new edition of this very useful book differs from its predecessor mainly in two features. Part I is new; it is a short treatise on the general principles of the practice, mainly by Dr. Allsopp. Part II constitutes a new and up-to-date edition of the original work, by Mr. F. Twyman.

The earlier section deals with the nature of absorption, illustrated by simple absorption spectra of various glasses, solvents, etc. In one chapter the Laws of Absorption and the Nomenclature of Absorption Spectrophotometry are considered. The well-known formulae for Lambert's Law and Beer's Law are discussed at length, the latter in much detail, with special reference to apparent exceptions; also an "Appendix" is devoted to the Algebraical Expression of Beer's Law. A chapter on Applications of Absorption Spectrophotometry and the Raman Effect opens with an interesting review of the earlier history of the subject, and leads on to a brief study of a few instances of both qualitative and quantitative applications of absorption spectra; the last is exemplified by the admirable work of Campbell Smith on serum proteins. Within the compass of a single page is given a good introduction to the Raman effect.

The later, larger section on "The Technique of Absorption Spectroscopy" deals with the instrumental equipment and with the scientific principles on which the many instruments are constructed. The "Spekker" spectrophotometer, which is usually, although not in this volume, described as the less costly offspring of an earlier and more elaborate model, takes now the leading place. The "Notched Echelon Cell," introduced in 1932, provides means for obtaining a series of spectra with one or two ml. of solution in half a minute. It gives all that is needed for a first absorption curve. Finally, a new photo-electric photometer is presented, for comparing the intensities of two spectrum lines. This, although primarily intended as an instrument of precision, will come as a great boon to many whose personal observations are uncertain, although others may be able to do trustworthy work without such aid.

The book will be welcomed by every one interested in absorption spectroscopy, whether from the standpoint of theoretical chemistry or from the industrial or other applied aspect. It brings before the reader some of the more remarkable of the many developments of method in a vast field of inquiry, which, in response to the new demands of workers on fresh problems, continues to enlarge its borders with a bewildering persistence.

The volume does credit to the producers; the print is clear and well arranged, while the several plates bring into good evidence the details to be demonstrated.

S. JUDD LEWIS

THE CARBOHYDRATES. By E. F. ARMSTRONG, D.Sc., Ph.D., LL.D., F.R.S., and K. F. ARMSTRONG, M.A., B.Sc. Fifth Edition. Pp. vi+252. London: Longmans, Green & Co. 1934. Price 15s. net.

Since the publication of the fourth edition of Dr. E. F. Armstrong's monograph, "The Simple Carbohydrates and the Glucosides," in 1924 (ANALYST, 1924, **49**, 497), great progress has been made in these branches of organic chemistry, and the work has now been published in two parts, of which one, "The Glycosides," appeared in 1931 (ANALYST, 1932, **57**, 481); the other forms the subject of the present review.

The vast amount of research on the sugars carried out during the past ten years is indicated by the long lists of references appended to each chapter, and the results of some of this research are so fundamental that it has been found necessary to re-write the book completely. Thus, ten years ago, the more stable (α- and β-) form of glucose was supposed to contain the butylene oxide ring structure and the less stable, so-called γ-glucose was supposed to contain the propylene oxide structure. The work of Haworth and his collaborators, however, has shown that the more stable glucose contains an amylene oxide structure and the less stable glucose contains the butylene oxide structure previously ascribed to stable glucose. Haworth has, therefore, designated these forms of glucose as (α- and β-) glucopyranose and (α- and β-) glucofuranose, thus indicating the relations between these sugars and the pyran and furan rings, respectively. Glucose is such an important building material in the carbohydrate edifice, that these new views as to its structure are of very wide significance. The corresponding isomers of fructose are named fructopyranose and fructofuranose and, according to Haworth, sucrose appears to be a compound of α-glucopyranose and fructofuranose. As is pointed out by the authors, however, the condensation of these compounds might give rise to ten different substances, and it is not surprising that sucrose has not yet been synthesised. The far-reaching importance of the new views concerning the structure of glucose and fructose is shown throughout the book, and especially in Chapter XV, which deals with the structures of the di-, tri- and tetra-saccharides. For this group of carbohydrates the authors have adopted the name "oligosaccharides," proposed by Freudenberg; it deserves to find general acceptance.

A very brief description of the polysaccharides is given in Chapter XVII as a supplement to the account of the simpler carbohydrates which occupies the first sixteen chapters. The two concluding chapters, dealing with the relation between configuration and biological behaviour and with the synthesis of carbohydrates in the plant, will be of special interest to the biochemist.

The earlier editions of this book by Dr. E. F. Armstrong formed extremely valuable epitomes of sugar chemistry and the same may be said of the new edition by Dr. Armstrong and his son; it is a masterly survey of our present knowledge of the subject. By the recent untimely and widely-mourned death of Mr. K. F. Armstrong this field of research has lost a worker of great promise.

LEWIS EYNON

VOLUMETRIC ANALYSIS. By H. P. STARCK, M.A. Pp. 228+31. London: Baillière, Tindall & Cox. 1934. Price 7s. 6d. net.

This is a students' book and is intended primarily to satisfy the requirements of the standard of University Scholarships, although a few pages at the end of each section are devoted to rather more advanced work for Intermediate and Final B.Sc. students. It follows the usual lines of such publications, and indeed, calls for little comment, being well-written and accurate. The author is without doubt best entitled to judge what should be included and what omitted; thus the chapter on *p*H values and the theory of indicators was a wise choice, and is well executed. At the same time, in view of the increasing importance of oxidation-reduction indicators, one would have expected to find some reference to them, especially as the use of diphenylamine is described under its appropriate reaction.

The up-to-date standard of the book is indicated by the inclusion of details for the use of tartrazine as an adsorption indicator, and it is a pity that rhodamine was not substituted here, as it is much better. Potassium iodate is referred to as an oxidising agent, but not as a means of standardising acids (for which it is extremely useful), and the method given for the determination of sulphites in glucose is quite unsatisfactory.

However, the book fulfils extremely well the main purpose for which it is intended, and the problems and answers (for which the author assumes complete responsibility) and appendix, containing the usual tables for qualitative analysis, should afford additional help to the student.

JULIUS GRANT

Publications Received

CLINICAL AND PATHOLOGICAL APPLICATION OF SPECTRUM ANALYSIS. By WALTHER and WERNER GERLACH. Translated by J. H. TWYMAN. Pp. 143. London: Adam Hilger, Ltd. 1934. Price 14s. 6d. net.

ELEMENTARY ANALYTICAL CHEMISTRY (CLOWES AND COLEMAN). By C. G. LYONS and F. N. APPLEYARD. Twelfth Edition. Pp. xii+242. London: Churchill & Co., Ltd. Price 6s.

QUANTITATIVE CHEMICAL ANALYSIS. By A. C. CUMMING and S. A. KAYE. Sixth Edition. Revised by F. C. GUTHRIE. Pp. xv+482. London: Gurney & Jackson. Price 15s. net.

TAYLOR'S PRINCIPLES AND PRACTICE OF MEDICAL JURISPRUDENCE. Revised by SIDNEY SMITH. With COMPLETE REVISION OF THE LEGAL ASPECT, by W. G. H. COOK. 2 Vols. Pp. 873 and 973. London: Churchill & Co., Ltd. 1934. Price 63s.

METHODIK DER VITAMINFORSCHUNG. By C. BOMSKOV. Pp. xvi+301. Leipzig: G. Thieme. 1935. Price M.24.

DIE RÖNTGENSPEKTROGRAPHIE ALS UNTERSUCHUNGSMETHODE. By J. R. KATZ. Abderhalden's Handbuch der Biologischen Arbeitsmethoden. Lief. 436. Berlin: Urban & Schwarzenberg. Price RM.20.

TESTING OF BITUMINOUS MATERIALS. By BROOME CHILD. London: Ed. Arnold. 1934. Price 15s.

CHEMISCHE GRUNDLAGEN DER LEBENSVORGÄNGE. By C. Oppenheimer. Pp. vii+298. Leipzig: G. Thieme. Price M.22.50.

THE SCIENCE OF RUBBER. Edited by K. MEMMLER. AUTHORISED ENGLISH TRANSLATION, edited by R. F. DUNBROOK and V. N. MORRIS. Pp. xvi+770. New York: Reinhold Publishing Co. 1934. Price $15.00.

PRACTICAL BACTERIOLOGY: AN INTRODUCTORY COURSE FOR STUDENTS OF AGRICULTURE. By A. CUNNINGHAM. Edinburgh: Oliver & Boyd. 1934. Price 7s. 6d. net.

AIDS TO THE ANALYSIS OF FOOD AND DRUGS. By C. G. MOOR and W. PARTRIDGE. Fifth Edition. Revised by J. R. NICHOLLS. Pp. 322. London: Ballière, Tindall & Cox. 1934. Price 5s.

INFLUENCE OF FERTILISERS ON THE NITROGEN AND CARBON CYCLES IN SOILS. By P. KAMERMAN and H. CLINTWORTH. Science Bull. No. 137, Union of South Africa. Dept. of Agriculture. Pp. 26. Pretoria. 1934. Price 3d.

UNION INTERNATIONALE DE CHIMIE: PREMIER RAPPORT DE LA COMMISSION PERMANENTE DE THERMOCHEMIE. 1934. Secrétariat Général: Rue des Mathurins, Parice.

ACHEMA JAHRBUCH 1931–1934. Pp. 152. Dechema: Seelze bei Hannover und Berlin. 1934. Price RM.10.

THE PHARMACOLOGICAL ACTION OF THE HARROGATE DRINKING WATERS. By W. BAIN. London: Churchill & Co., Ltd. 1934. Price 5s.

EINFÜHRUNG IN DIE ORGANISCH-CHEMISCHE LABORATORIUMSTECHNIK. By K. BERNHAVER. Berlin: J. Springer. 1934. Price RM.4.80.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 6th, Mr. John Evans, President, being in the chair.

Certificates were read in favour of:—Albert Edward Andrews, A.I.C., William Lewis Davies, Ph.D., M.Sc., F.I.C., George William Ferguson, B.Sc., Ph.D. A.I.C., Oswald Hitchen, B.(Tech.)Sc., A.I.C., John Knaggs, B.Sc., Ph.D., A.R.C.S., D.I.C., F.I.C., Norman Ratcliffe, F.I.C.

The following were elected members of the Society:—Henry Dryerre, Ph.D., M.R.C.S., L.R.C.P., Ronald William Hoff, A.R.C.S., A.I.C., Laurance John Sidney Lane, B.Sc., Alfred Edward Wright.

The following papers were read and discussed:—"The Chemical Examination of Furs in Relation to Dermatitis, Part V, The Action of Acid on Bandrowski's Base," by H. E. Cox, D.Sc., Ph.D., F.I.C., and J. U. Lewin, B.Sc., F.I.C.; "The Use of Infra-Red Rays in the Examination of Inks and Pigments," by C. Ainsworth Mitchell, M.A., D.Sc., F.I.C.; and "Vitamin Potency and Associated Characteristics of Cod-liver Oil," by R. S. Morgan and H. Pritchard.

NORTH OF ENGLAND SECTION

The Tenth Annual General Meeting of the Section was held in Manchester on February 9th, 1935. The attendance was thirty-six; the Chairman (Prof. W. H. Roberts) presided.

The Secretary read the report and financial statement for 1934, which were adopted.

The following appointments for the coming year were made:—*Chairman*, Prof. W. H. Roberts; *Vice-Chairman*, A. R. Tankard; *Committee:* Prof. T. P. Hilditch, A. O. Jones, C. H. Manley, H. M. Mason, A. Scholes, C. J. H. Stock, R. W. Sutton; *Honorary Auditors:* U. A. Coates, J. W. H. Johnson; *Honorary Secretary and Treasurer*, J. R. Stubbs.

The following papers were read and discussed:—"Difficulties in Determining the *p*H values of Various Liquids," by D. Burton, M.B.E., D.Sc., F.I.C.; "The Determination of Water in Foodstuffs," by H. M. Mason, M.Sc., F.I.C.; "The Determination of Moisture in Cereal Products by Distillation with Tetrachloroethane," by J. M. Tucker, B.Sc., F.I.C., and T. E. Burke, A.I.C.

Death

WITH great regret we record the death of Frank Edward Day, who joined the Society in 1913.

Obituary

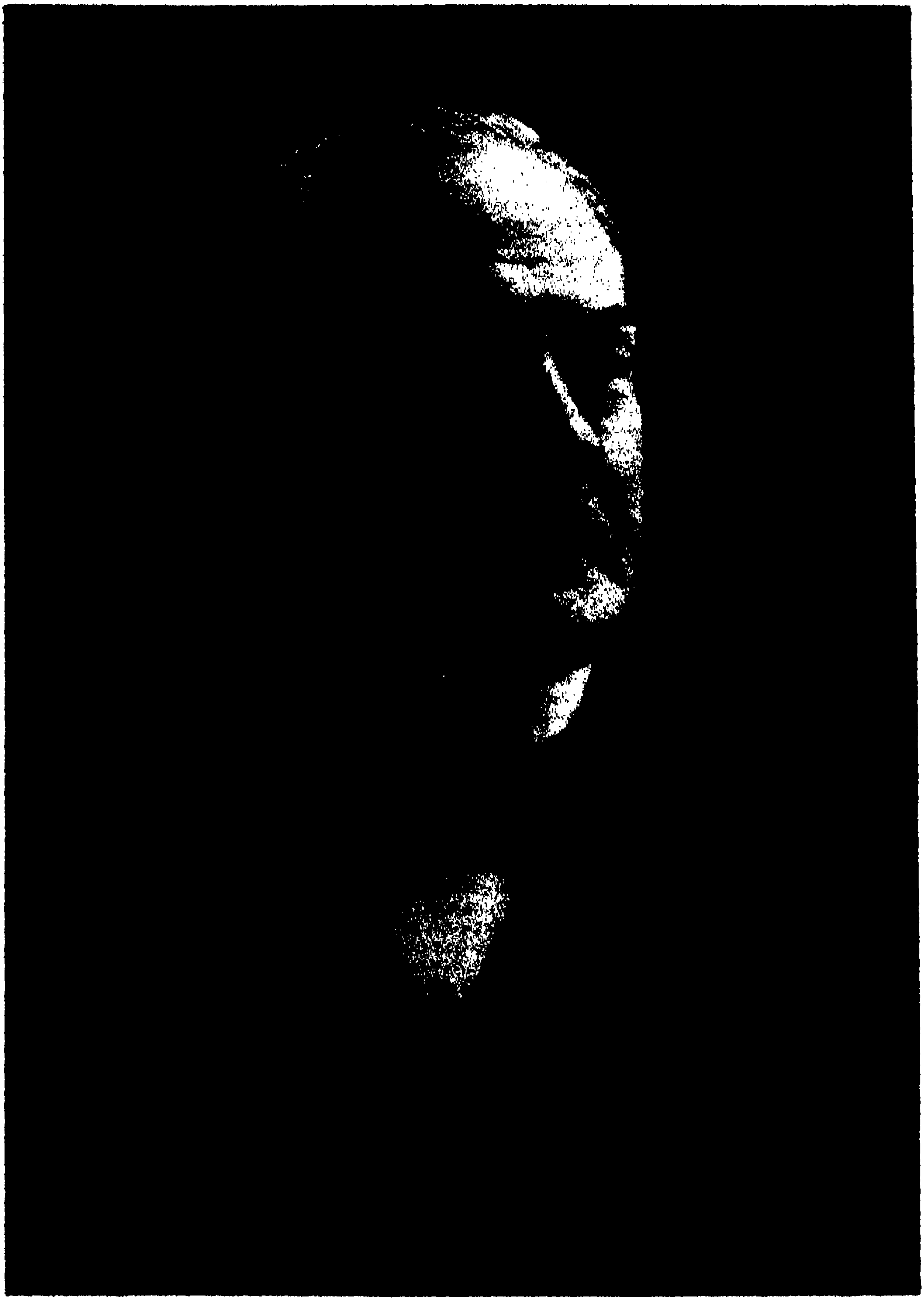
ROBERT RATTRAY TATLOCK

ROBERT RATTRAY TATLOCK was born in Glasgow on May 18th, 1837, and died at Helensburgh on December 22nd, 1934. He was the elder son of Robert Tatlock, a manufacturer in Glasgow, and on the maternal side he could trace his ancestors, who were engaged in commerce, back to the early years of the seventeenth century.

Tatlock received his early education in Greyfriars' School and later in the Trades House School, but from his youth his aim was to be an analytical chemist, and his motto was that he must excel in his chosen science, or leave it alone. With this object in view, he studied chemistry under Dr. Penny in Anderson's College (the site of which is now occupied by the Glasgow Royal Technical College), and later he was appointed chief assistant to Dr. Penny, a post which he held for over eight years. During this period, perhaps his most important undertaking was the analysis of over 100 "productions" in the trial for the murder by Dr. Pritchard of his wife and mother-in-law. This investigation was carried out entirely by Tatlock, the result being that antimony was found in quantity, having been administered in the form of tartar emetic.

About 1865 Tatlock severed his connection with Anderson's College, and accepted the post of manager in one of the departments of the Kames Gunpowder Company, Kyles of Bute. He remained in this post for only a short period, and in 1867 began his career as an analytical and consulting chemist in a laboratory in George Street, a short distance from Anderson's College. There success came slowly but surely; it was gained only by determination and very hard work, as those well knew who were intimate with him. In addition, he had classes for students, one of whom, in 1869, was the late Sir William Ramsay. In 1909 Ramsay wrote a short autobiography, in which he said: "In 1869 I entered the laboratory of Robert Tatlock, who had been assistant to Professor Penny. Mr. Tatlock was (and is) an eminent analytical chemist, and during a year with him I had a course of qualitative analysis, and got through a good part of quantitative analysis."

In 1868 Tatlock read his first paper on analytical chemistry before the Chemical Section of the Glasgow Philosophical Society. This was "On the Estimation of Potassium," and was the result of a laborious series of trials in collaboration with his friend James Chalmers, who was also an excellent chemist. They came to the conclusion that the results reported by some chemists were too high in potassium, and they traced this to the fact that considerably different atomic weights for platinum were in use. Working on chemically pure potassium chloride, they found that the atomic weights required to obtain an accurate result were those



R.R. Tatlock

published by Stas in 1865. They were: platinum, 197·193; potassium, 39·137; chlorine, 35·457. These results, which have been corroborated by other analysts, mean that if the International Atomic Weights for 1934 are adopted, the result would be 100·36 per cent. for pure potassium chloride. The new atomic weights are: platinum, 195·23; potassium, 39·096; chlorine, 35·457; the last is identical with Stas's figure of 70 years ago, while that of platinum has been oscillating. Tatlock had his results re-tested and confirmed, and, to the last, adhered to the old atomic weights.

Another pet subject of Tatlock's was that of graduated vessels used in chemical analysis, and indeed he was almost finical about them. He had an apparatus by which a tube (a burette for example), although of unequal calibre throughout, could be graduated so that each division delivered exactly the same volume of the same fluid. In 1870 he read a paper on "Some Sources of Error in Volumetric Analysis," dealing with this subject.

In 1870 Tatlock joined in partnership with Dr. William Wallace and Dr. John Clark, both of them eminent analysts, under the designation of Wallace, Tatlock & Clark. The firm was dubbed the "Chemical Trinity" by *The Bailie*, a Glasgow comic weekly. They proved to be a very strong combination, and practically monopolised all the analytical work required in the City of Glasgow.

A good deal of work was done on the analysis of Scottish blackband and clayband ironstone, but this source of iron gradually dwindled, and Spanish iron ore began to be imported. Tatlock managed to obtain the sampling and analysis of these ores, and in time it formed a large part of the analytical business, which has continued, with ups and downs, especially the latter, in recent years. Happily for the iron trade in Scotland, improvement has begun. Tatlock was the first to undertake this work in Scotland, and, like everything he took in hand, he carried it on to success.

In 1877 he was, along with his partners, appointed Public Analyst for Glasgow, and he held that post till his death. In 1888 he dissolved the partnership with Wallace and Clark, and joined with Dr. J. B. Readman, an Edinburgh analyst well known at that time, the new firm being R. R. Tatlock & Readman, and on Dr. Readman's retiral, the firm of R. R. Tatlock & Thomson was formed. In 1888 Tatlock was appointed Gas Examiner to the City of Glasgow.

During these co-partneries, and later, the usual routine work of a laboratory was carried on, but there were four outstanding matters to attend to. In 1896 Tatlock was appointed Sewage Analyst to the Corporation of Glasgow, the object being to determine the method of treatment that would be most suitable, when all the circumstances were taken into account. Shortly before the Boer War he was requested to go to South Africa, and at Pretoria he gave expert evidence in favour of the Macarthur–Forrest process for the extraction of gold from ores by potassium cyanide. He was also employed to give evidence for Nobel's Explosives Co. in their case, "Ballistite *v.* Cordite," against H.M. Government.

The fourth important business was to give evidence before the Royal Commission which was appointed, in 1907, to answer the question "What is Whisky?" This arose out of cases in which prosecutions were instituted against samples that were not up to the standard in secondary products for pot-still whisky. It was assumed that the pot-still variety only was genuine whisky, although the patent-still product had been in use for 73 years, and was always called whisky. Another point was that a rumour went about that patent-still whisky was poisonous, and a chemist, who shall be nameless, said that he gave pot-still whisky to one monkey and patent-still whisky to another, the result being that the former became benevolently drunk, and the latter beastly drunk. Tatlock experimented upon himself, but neither of these results occurred. The Royal Commission decided in favour of the distillers, and left matters as they were.

Tatlock also contributed a number of papers to THE ANALYST and other publications, such as those on Tea, Coffee, Water, etc., and one on "The Determination of small proportions of Bromine and Chlorine in Iodine," this being a subject in which he was much interested.

From 1873 to 1884, besides attending to his duties in the laboratory, Tatlock lectured on chemistry in the College of Science and Arts, now incorporated in the Royal Technical College. He did not profess to be an orator, but the clearness and precision of his exposition of the principles of chemistry could not be surpassed. He was particularly careful in the preparation of his experiments shown on the lecture table, and they never failed to come off. At the beginning of a course, he always gave several lectures on physics, dealing with sound as well as with heat and electricity. As an example of his minute care about experiments, the well-known singing flames may be taken. He had three or four which gave different sounds, and adjusted the surrounding tubes exactly on the points where they gave a sound at a certain pitch. He then struck the required note on a violin and immediately the flame responded and sang, as we say in popular language.

In 1867 he was elected Fellow of the Chemical Society, in 1870 Fellow of the Royal Society of Edinburgh, in 1877 Fellow of the Institute of Chemistry, and in 1903, when the Association of Public Analysts of Scotland was formed, he was elected first President. From 1888 to 1890 he acted as Examiner in the University of Glasgow. He became a member of the Society of Public Analysts in 1876, served on the Council in 1887–8 and 1904–5, became Vice-President in 1891–2, and was elected President in 1908–9.

Tatlock loved his work, and was thorough, perhaps excessively so, in preparing his evidence for important cases, but he did not lose by such care. He would not only prepare arguments for his own side, but would also discuss any the other side might bring forward. As an example, in one case at a meeting with Counsel, he gave his facts and arguments for his clients, and then was asked what evidence he would give against them. He did so, and Counsel told him that he should be on the other side, and that, their case being bad, it would be advisable to admit liability and settle the matter out of Court.

Outside his profession he was excellent company, and had always some good stories to tell, but when in a somewhat flippant mood he would talk nonsense for fun. On one such occasion, one of his best friends, a brother analyst, told him that he was the most frivolous man he ever knew. He certainly loved to talk nonsense sometimes, but that is really a saving grace in a serious-minded man like him.

Tatlock was no specialist in the narrow sense of the word, for, to the last, he took an interest in politics, music and literature. In politics he held liberal principles, but was not a rigid party man, and recently he described his views as those of a sensible socialist, but he never took any active part in politics.

In his earlier days he was an excellent violinist, being very fond of music, and in his later days, when he could not go to concerts, he listened to them on the wireless. He specially loved Scots songs, and even when going round the laboratory among his assistants he would be singing some melody in a low crooning voice.

Tatlock had the courtly manners towards others that we called the conduct of a gentleman, the true meaning of which is lost in our more unconventional age. He was no hero worshipper, but towards Faraday he came very near that attitude. He admired his great work as a chemist, but he could never forget a Sunday in a little Glassite Chapel in Glasgow, when he heard Faraday preach a simple and beautiful sermon on "Let brotherly love continue."

Tatlock is survived by a son and by a daughter—the wife of the Very Rev. Charles Warr, Dean of the Thistle.

May I close on a personal note? For about 50 years I was in daily business relations with Tatlock, and during all that time we worked harmoniously together, without a note of disagreement—a record, he used to tell his friends. Then in his retirement we kept up the old friendly relations, and to the last he took an intense interest in our business and in all that went on in the chemical world.

R. T. THOMSON

The Question of Tannin in Maté

By W. A. WOODARD and A. N. COWLAND

(WORK DONE UNDER THE SOCIETY'S ANALYTICAL INVESTIGATION SCHEME)
(*Read at the Meeting, December* 5, 1934)

INTRODUCTION.—In South America and associated countries a beverage is made from maté, the dried leaves of various species of *Ilex* (Fam. *Aquifoliaceae*)—shrubs indigenous to Brazil and Argentina. It is usual to take the drink as an aqueous infusion, prepared in a silver cup or gourd, from which the name "maté" is derived.

Owing to the discovery of the shrub in Paraguay by early Jesuit missionaries in the seventeenth century, all varieties of maté, irrespective of species, have come to be known as *Ilex paraguayensis*. The genus *Ilex*, however, contains two-hundred-and-eighty species, and Wehmer[1] gives the names of nine different varieties of *Ilex* leaves sold under the name of maté. To-day, the finest variety obtainable is derived from *Ilex paraguariensis* (St. Hilaire), and in Parana it is forbidden by law to export any other.

The process for curing maté is distinct from that used for common "tea"; moreover, it is unlikely to produce any appreciable change in the phenolic constituents of the plant. Tea is rolled and fired, maté is not. In several publications it is stated that maté is dried by means of smokeless heat.*

According to the descriptions given in abstracts from this literature and elsewhere the modern curing process may be summarised roughly as follows:—The twigs and leaves are collected between May and September, this period being fixed by law to avoid damage to the shrubs. First, there is a preliminary toasting and drying by means of hot air; direct heat is carefully avoided, because smoke would give the finished product an undesirable taste and odour. Secondly, after a definite period of storage, the leaves and twigs are separated by means of a special threshing process. Lastly, the leaves are subjected to a final drying by means of hot air conveyed through pipes or tunnels. The final product should be green, hard and resistant to fermentation and deterioration.

The presence in maté of so-called tannin, either identical with, or analogous to, that in tea, has been definitely reported by several chemists, but it should be pointed out that little or no work has been done on the phenolic constituents of the drug since 1922. This was before the advent of such specific tests as that requiring the use of goldbeaters' skin, and we have therefore made a critical examination of the results of earlier work. The more important references are as follows:—Rochleder and Hlasiwetz[2] concluded that the main phenolic constituent of maté was identical with the caffetannin of coffee. Arata[3] found the plant phenol to be analogous to, but not identical with, that of coffee. Peckolt[4] published a confirmation of Arata's work. Kunz-Krauze[5] described the main constituent as a glucoside of either caffeic or chlorogenic acid containing an unknown optically inactive hexose. Peacock and Peacock[6] concluded, on very slender evidence, that maté contained an astringent principle which they isolated and identified as a phlobaphene.

At the suggestion of the Society's Analytical Investigation Scheme Committee we have made a further investigation, dealing primarily with the question of the presence of genuine tannin; secondary considerations were the establishment of a difference between the plant phenols of maté and common "tea" and an attempt to separate colouring matter from the main plant phenol in maté, with the object of obtaining data relating to their constitution and structure.

Preliminary Examination.—Thirty individual samples of cured maté were examined, including imports dating as far back as 1920 and 1927, as well as current imports from wholesale houses and purchases from London stores. A cursory botanical examination showed that all the samples were typical of the genus *Ilex*, although there was undoubtedly some variation in species.

A small and limited supply of each kind of maté for comparison purposes was obtained by courtesy of the authorities at Kew. Coffee beans (*Coffea arabica*) and Asiatic tea leaves (*Thea chinensis*) were also compared with maté, with a view to bringing out essential similarities and differences. Except in certain instances, aqueous extracts (1 in 20) were used for the tests. The extracts were prepared by decocting the comminuted material with water for fifteen minutes; when necessary, chlorophyll, caffeine, fats, waxes, resins, etc., were removed by treatment with organic solvents.

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* "Maté: An Important Brazilian Product," by C. R. Cameron (*Bulletin of the Pan-American Union*, Oct., 1929, pp. 988–1005); "Il Mate o Tè del Paraguay," by Dr. C. Micastro (*L'Agricoltura Coloniale*, Nov., 1928, to Aug., 1929); "A Exploracao do Mate" (*Boletin do Ministerio da Agricultura, Industria e Commercio*, Brazil, for April and May, 1929).

It will be realised by those familiar with the analysis of tannins that the available tests capable of giving specific results are very few. In this work, particular emphasis has been laid on the results obtained with goldbeaters' skin,[7] gelatin solution, and certain tests devised by Ware, all of which, with certain exceptions, are described in *Allen's Commercial Organic Analysis*, Volume V, under the section dealing with tannins.[8] It was found necessary to employ a limited number of colour reactions, but only those were used with which it was considered possible to carry out control tests.

Aqueous extracts of maté had the following general characteristics:—Yellowish-brown in colour, giving an acid reaction to litmus (pH 5 to 6); they gave precipitates with solutions of cinchonine and quinine sulphates and a copious yellow precipitate with basic lead acetate; ferric iron (with increasing pH) gave a grass-green colour, whereas ferrous iron (with carefully controlled decreasing pH) gave green, violet, purple and deep brown colours; aqueous ammonia (10 per cent.) gave a beautiful emerald-green which deepened rapidly on shaking or allowing the mixture to stand in contact with air.

The reactions with iron salts were particularly interesting, especially when considered in conjunction with the results of tests for genuine tannin detailed in the next section of this paper. The results given with ferrous iron (Mitchell's ferrous tartrate reagent)[9] have special significance when interpreted according to Ware.[10] Ware[11] classified plant phenols by the colours and precipitates obtained with the ferrous tartrate reagent in the presence of an appropriate quantity of $N/50$ sodium bicarbonate solution or a weak solution of ammonia; if no colour is obtained, the phenol is provisionally assigned to class A; a violet colour indicates probably a phenol of class B, and a deep brown colour probably a phenol of class C.

Maté extracts gave results typical of classes B and C; the more important phenols belonging to class B are pyrocatechol, protocatechuic acid, the catechinols (catechins), chlorogenic acid, caffetannin, ipecacuanhic acid, adrenalin and catechol tannins; class C (containing most of the pyrone and quinonoid phenols, and some benzophenone phenols) is represented chiefly by the anthoxanins, such as the flavone, luteolin, and the flavonols morin, quercetin, quercetrin, rutin, myricetin, etc.

It is not practicable to set out here in full all the tests used to show the absence of various phenols from maté; it is sufficient to state that the following substances were thoroughly tested for, particular attention being paid to the possible presence, in the free state, of the first two in the list:—Gallic acid, catechol, protocatechuic acid, resorcinol and phloroglucinol. There was no evidence indicating the presence, in the free state, of any of these substances.

Another qualitative reaction of extracts of maté is the beautiful emerald-green colour obtained with ammonia. We believe this reaction to be characteristic of maté, and probably of caffetannin; the colour is very intense, persisting for several hours and slowly changing, on long contact with air, to a deep brown. This is undoubtedly an oxidation reaction, because the colour can also be obtained with acid permanganate, and, conversely, can be completely and rapidly destroyed by reduction with zinc and hydrochloric acid. Aqueous extracts of coffee beans gave a similar reaction, but the colour was very much less intense.

It is well known that, under suitable conditions, many phenols (notably gallic acid, gallotannin, catechol, protocatechuic acid and resorcinol) will give a green colour with ammonia or other alkali, but the colour is usually very transient and much less intense than that given by maté extractives; moreover, it must be recalled that four of the above-mentioned substances have been shown by many tests to be absent from maté.

There has been a general tendency in the past to associate chlorogenic acid with this peculiar green colour given by various extracts with ammonia solution; furthermore, it has been customary to identify caffetannin with chlorogenic acid, in spite of the fact that the evidence for their identity is very slender. Nierenstein,[12] dealing with hydrolysable tannins, gives good reasons for the conclusion that caffetannin and chlorogenic acid are not identical. Gorter,[13] describing the reactions of chlorogenic acid isolated from coffee, makes it clear that it gives with ammonia not a green colour, but a definite yellow which, on standing, acquires a reddish tint.

The preliminary examination of maté extracts indicated the presence of two plant phenols, *viz.* an iron-greening anthoxanin (probably a flavone or flavonol derivative) which was responsible for the deep brown colour given with Mitchell's reagent in the presence of sufficient alkali; and secondly, what is here described as a pseudo-tannin (probably a caffetannin), which gave the violet colour with Mitchell's reagent, also in the presence of sufficient alkali; appreciable quantities of these two phenols undoubtedly exist in maté. As will be seen, the results recorded at a later stage of this work tend to substantiate this suggestion.

EXAMINATION OF FRESH AND CURED MATÉ FOR TANNIN.—The more important results are given below in tabular form, the tests used being all fairly well known, with, perhaps, the exception of the antipyrine test devised by Ware.[14] This routine test for tannins, used in conjunction with a suitable phosphate buffer, gave excellent results with controls containing very small amounts of gallotannin.

TABLE I

Test	Observation	Inference
Goldbeaters' skin		
(*a*) Treatment for tanning	No opacity	Tannin absent
(*b*) Staining with ferrous sulphate	Greyish-green stain	Indication of iron-greening anthoxanin
(*c*) Decolorisation with acid	No final stain	Phlobaphen absent
Gelatin solution	Complete absence of turbidity or precipitate	Tannin absent
Ware's antipyrine test	No turbidity or precipitate	Tannin absent
Ware's iron and ammonium citrate test	No precipitate	Tannin absent
Ware's modification of Stiasny's reaction	No characteristic precipitate	Phlobatannin absent
	Iron-greening and iron-browning filtrate	Gallotannins absent
	No blue colour produced	
Ware's modification of Mitchell's ferrous tartrate test	No blue or violet colour produced	Gallotannin absent

In addition to the tests described above, a hide-powder test, kindly made by Dr. E. W. Merry of The British Leather Manufacturers' Research Association, gave noteworthy results. The comminuted material (25 g.) was extracted with 1 l. of water in a Procter extractor at a temperature not exceeding 60° C. The sample contained 33·2 per cent. of water-soluble substances, of which 12 per cent. was absorbed by the hide powder, as used in the official method of tanning analysis; the remaining 21·2 per cent. was not absorbed. Lack of sufficient fresh material made it impossible to make a control test; but since hide powder will absorb substances other than tannins, including natural colouring matters and non-volatile organic acids, we suggest that the absorption in the case of maté was due to the presence of one or both of these constituents in the leaves of the plant.

The results of sensitive spot-tests on filter-paper, devised by Ware,[15] confirmed the foregoing conclusions; the same author's tests with iodine and ammonia were also confirmatory.

It is noteworthy that the goldbeaters' skin test, the most specific test known for detecting genuine tannin, gave a negative result with each of the thirty samples of maté examined. We conclude that there is not, and never has been, any genuine tannin in maté, for the following reasons:

(*a*) First and foremost there is no phlobaphen present.
(*b*) There is no gallic acid present.
(*c*) The modern process by which the leaf is cured is unlikely to produce tannin or to destroy it.

A COMPARISON OF FRESH MATÉ WITH FRESH TEA.—These tests bring out certain pronounced differences between maté and tea. Little can be said about the plant phenols in tea, because the chemistry of tea-tannin is a mass of contradictions and requires further elucidation. Comparisons were also made with fermented tea, but the results were so similar to those given in Table II that there was no point in recording them. The only noticeable difference between fresh and fermented tea was that the cured material gave strong positive results for phlobaphen, whereas the fresh tea did not.

It is clear from these results that, so far as qualitative tests go, there is little similarity between maté and tea. Tea undoubtedly contains genuine tannin, but maté does not, and this constitutes the chief and most far-reaching difference between the two.

A COMPARISON OF FRESH MATÉ WITH FRESH COFFEE.—These tests bring out differences and similarities between maté and coffee. A comparison of the cured materials also gave very similar results, except that with coffee the reactions were much less intense; this was probably due to destruction of plant phenols during roasting.

Coffee beans are known to contain caffetannin and chlorogenic, caffeic, and gallic acids. From the comparison given on p. 140 it seems probable that a little genuine tannin is also present; this would be quite feasible, since it is rare to find gallic acid unassociated with tannin in a plant. It is noteworthy that the remarkable reaction with ammonia (p. 137) is also shared by extracts of coffee.

TABLE II

Test	Observation	Inference
Goldbeaters' skin	Maté: Already described.	—
	Tea: Definite opacity with bluish-green stain	Tannin present; gallotannin, gallic acid or catechol tannin present
Gelatin solution	Maté: Already described	—
	Tea: Characteristic precipitate	Confirmation of presence of tannin
Ware's modification of Stiasny's reaction	Maté: Already described	—
	Tea: Characteristic precipitate, iron-blueing and iron-greening filtrate	Phlobatannin present: gallotannin, gallic acid or catechol tannin present
Osmium tetroxide solution (1 per cent.) + appropriate buffer	Maté: Reddish-brown, no violet or blue	Confirmed absence of gallic acid
	Tea: Purplish-violet	Probable presence of a pyrogallol tannin
Bromine water	Maté: No precipitate on standing	Absence of catechol tannin
	Tea: Precipitate on standing	Probable presence of catechol tannin
Nierenstein's test (0·5 per cent. diazobenzene chloride)	Maté: No precipitate on standing	Absence of catechins or catechol tannin
	Tea: Precipitate on standing	Presence of one, or both, of these substances

SEPARATION OF THE PLANT PHENOLS IN MATÉ.—The preliminary examination of maté extracts indicated the presence of two plant phenols: one classified as a pseudotannin, and the other as a member of the large family of natural yellow colouring matters. Perkin[16] has called attention to the fact that many natural colouring matters and tannins associated in plants often show a marked resemblance to each other in constitution and chemical reactions. This seemed probable with

TABLE III

Test	Observation	Inference
Goldbeaters' skin	Maté: Already described	—
	Coffee: Slight opacity, bluish-green stain	Indication of a little tannin; gallotannin, gallic acid or a catechol tannin present
Solution of gelatin	Maté: Already described	—
	Coffee: Slight turbidity	Confirmation of above result
Ware's modification of Stiasny's reaction	Maté: Already described	—
	Coffee: Very slight precipitate, iron-greening and iron-blueing filtrate	Confirmation of above results
Ammonia solution, 10 per cent.	Maté: Beautiful emerald-green intensified on shaking	Caffetannin present
	Coffee: Very similar to maté only less intense	Caffetannin present
Osmium tetroxide solution (1 per cent.) + appropriate buffer	Maté: Already described	—
	Coffee: Same as maté, but tinged with violet	Probably a little gallic acid or tannin present
Nierenstein's test (0·5 per cent. diazobenzene chloride)	Maté: Already described	—
	Coffee: No precipitate on standing	Absence of catechins and catechol tannin

maté, since the reactions of one phenol nearly always tended to be masked by those of the other.

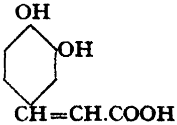
For this reason attempts were made to separate the two constituents. Fractional precipitation with lead gave poor results; various attempts to remove the colouring matter by adsorption or oxidation were equally unsuccessful. Extraction with different organic solvents yielded, towards the end of the work, some measure of success. It was noticed that neutral acetone extracted some colouring matter from maté, but very little or no pseudotannin; alkaline acetone extracted a fair amount of colouring matter, but again, little or no pseudotannin; acidified acetone extracted both plant phenols in sufficient amount to afford hope of a good separation when the extract was treated with dry ammonia gas for a definite period. The process actually used was briefly as follows:

One kg. of dried and powdered maté was allowed to stand in contact with dry chloroform for six hours with occasional shaking. The chloroform was then decanted, and the leaves were pressed; washing with several portions of ether and a final pressing of the leaves completed the removal of caffeine, chlorophyll, fats, resins, waxes, etc. It goes without saying that the plant phenols in maté had previously been found to be almost insoluble in chloroform and ether. Next, the pressed material was spread out on a tray and dried at a temperature not exceeding 60° C. Treatment with acidified acetone followed (*p*H 3 to 4, adjusted by means of concentrated sulphuric acid), sufficient solvent being added to cover the leaves completely, and twenty-four hours being allowed for the extraction. The solution was filtered through a Buchner funnel, and a fairly rapid current of dry ammonia gas was passed through the filtrate for about two minutes. The pinkish-red precipitate obtained was quickly washed with neutral acetone (several times), and then transferred to a desiccator to dry. The filtrate, containing colouring matter, was again treated with ammonia gas, any precipitate obtained being neglected; after re-filtering, if necessary, the new filtrate was evaporated to dryness under reduced pressure, and the residue was transferred to a desiccator.

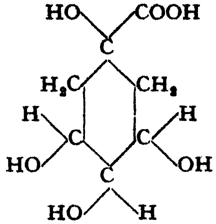
This represents a rough attempt to separate the colouring matter from the plant phenol or pseudotannin, but the method will probably need some re-adjustment before being applicable on a large scale.

EXAMINATION OF THE PRECIPITATE.—The precipitate obtained by the method described had the following general characteristics:—It was readily soluble in water, forming a clear reddish-brown solution; the reaction to litmus was markedly acid, and the colour given with ammonia was the deep emerald-green already described; ferric iron (with increasing *p*H) gave a grass-green colour, whereas ferrous iron (with decreasing *p*H) gave green, violet-purple, and finally a deep wine-red colour, but no brown colour was noticed. According to Ware,[11] this reaction is typical of pseudotannins in general. Precipitates were obtained with cinchonine and quinine sulphates, heating by itself yielded catechol, and fusion with alkali gave catechol together with a volatile acid not yet identified. It is worth noting that the preliminary reactions for colouring matter, and also others described later in detail, gave negative results when applied to an aqueous solution of the above precipitate.

Caffetannins give, on hydrolysis, (i) caffeic and (ii) quinic acid, and a residue not yet fully investigated.

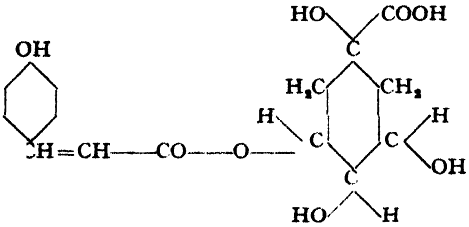


(i) Caffeic acid



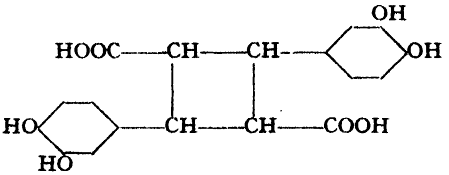
(ii) Quinic acid

Nierenstein (*loc. cit.*) is in favour of regarding caffetannin as a condensation product of (iii) chlorogenic acid, the established formula of which is given below.

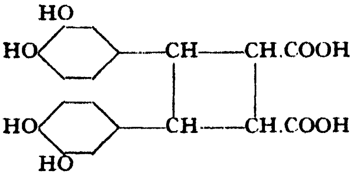


(iii) Chlorogenic acid

If this view be accepted, the residue obtained on hydrolysis would be either (iv) tetrahydroxy-truxillic acid or (v) tetrahydroxy-truxinic acid.



(iv) Tetrahydroxy-truxillic acid



(v) Tetrahydroxy-truxinic acid

At present little is known of either of these acids; moreover, Nierenstein[12] points out that in accepting the suggested formula for caffetannin it must be realised that the production of caffeic acid would be entirely due to the presence of some unchanged chlorogenic acid in the caffetannin. Finally, he agrees with Gorter,[13] who is of the opinion that caffetannin is a mixture of several substances, including chlorogenic acid.

An attempt was made to produce caffeic acid from the precipitate obtained from acidified acetone. The precipitate was treated with a slight excess of 10 per cent. aqueous potassium hydroxide solution and hydrolysed under reduced pressure for thirty minutes; after cooling, the brown solution was acidified with dilute sulphuric acid and then shaken out with several portions of ether. The ethereal layers were mixed, the solvent evaporated, and the residue was taken up in a little water. This aqueous solution gave positive results in the following tests devised by Gorter[13] for caffeic acid obtained by him from coffee beans: a grass-green colour with weak ferric iron solution; a lemon-yellow colour with lead acetate solution and baryta water; ready reduction of silver nitrate, and a yellow colour with ammonia solution, changing to a reddish tint on standing. This last reaction is also shown by chlorogenic acid.

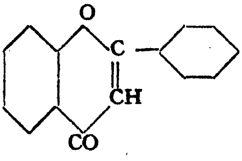
The same tests were applied to a residue obtained by a method proposed by Griebel[17] for determining chlorogenic acid in coffee. The method depends on the conversion of chlorogenic acid into caffeic acid by alkaline hydrolysis; the results were positive for caffeic acid.

An attempt to produce quinic acid from the precipitate under discussion was based on the knowledge that this substance, when distilled with sulphuric acid and manganese dioxide, yields quinone. The precipitate was hydrolysed with excess of 30 per cent. aqueous potassium hydroxide solution for one hour; subsequent distillation with concentrated sulphuric acid and manganese dioxide, gave, on standing, a yellow deposit which was collected and identified as quinone.

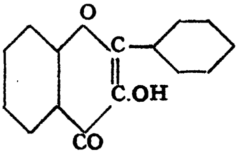
We fully realise that the results just described need further confirmation; nevertheless, we maintain that there is, at this stage of the work, evidence for concluding that caffetannin, or some closely allied substance, is present in maté. As previously mentioned, the search for a practical method of separating the two phenols in maté has only recently been successful, and work is still in progress with the object of obtaining the pseudotannin and colouring matter in the crystalline state. Attempts were made to crystallise the pinkish-red precipitate described above, but the final product was invariably a hard brittle mass. This may have been due to impurity, or, on the other hand, possibly the precipitate is a mixture of substances; if so, this would be another point in favour of caffetannin being present.

Another possibility is that chlorogenic acid exists in the free state in maté. The tests described by Charaux[18] and by Gorter,[19] depending on colour reactions with iron salts after acid hydrolysis of fresh extracts, gave results indicating the presence of chlorogenic acid. Hoepfner[20] describes a colorimetric method for determining chlorogenic acid in coffee; this was tested with maté, coffee being used as a control, and the result was positive. In spite of this, we think that it is difficult to state definitely whether the reactions just described would be given by chlorogenic acid existing in the free state in maté, or by the same acid existing as a component of a mixture such as caffetannin may be. This must be left for further investigation.

Examination of the Filtrate.—The presence of an iron-greening anthoxanin, probably a (vi) flavone or (vii) flavonol derivative, was indicated by the results obtained in certain tests in the preliminary examination.



(vi) Flavone



(vii) Flavonol

Attention has been called to the fact that the reactions of one phenol interfered with those of the other; owing to this confusion, it was thought at one time that the colouring matter in maté was almost çertainly a flavonol derivative, but the separation process has made it possible to correct this error.

The filtrate from the acid acetone precipitate should contain the colouring matter; a residue obtained from such a filtrate in the manner already described, gave the following general reactions: It dissolved in water to give a pale yellow solution, being slightly acid to litmus and giving a copious yellow precipitate with lead acetate; with ferric iron (increasing *p*H) a green colour was obtained; with ferrous iron (decreasing *p*H) there was a green colour, which, on adding sufficient *N*/50 sodium bicarbonate solution, became deep brown; no violet or purple colour was seen, thus indicating, according to Ware,[11] that phenols belonging to class B had been eliminated; in other words, plant colouring matter had been separated from pseudotannin. When heated alone, the dry residue gave catechol; when fused with alkali, it gave protocatechuic acid and phloroglucinol.

The following results, presented in tabular form, sum up the more important reactions of the colouring matter in maté.

TABLE IV

Test	Observation	Inference
Calico or wool mordanted with aluminium	Bright yellow—no reddish tint—fairly fast to light; fluoresced in ultra-violet light	Flavone or flavonol present; probably a flavone
Ware's iron and ammonium citrate test	Production of a heavy brown precipitate	Presence of a catechol, phloroglucinol, flavone or flavonol
Willstätter's reduction reaction	Complete absence of any colour	Flavonols absent; flavone derivative probably present
Perkin's test (air-oxidation of an alkaline solution, followed by acid precipitation)	Definite precipitation after acidification	Flavone derivative present

All natural hydroxyflavones dye fabrics mordanted with aluminium a yellow shade, the intensity of which is dependent upon the position of their hydroxyl groups. The yellow given by flavonols to mordanted calico is usually slightly tinged with red, which serves as a useful distinction from flavones. Willstätter's reduction test with zinc and hydrochloric acid is another useful reaction for distinguishing flavones from flavonols. A third reaction, based on Perkin's observation that hydroxyflavones are not, as a rule, readily oxidised in alkaline solution, serves as a useful confirmatory test. The tests for colouring matter in maté were controlled with oak-bark containing quercetin and onion-skin containing apigenin.

We thus consider that there is good evidence pointing to the existence in maté of a flavone derivative. In further work it is hoped to obtain confirmation of this by preparing the colouring matter in the crystalline state and investigating its chemical constitution.

CONCLUSIONS.—It has been shown that maté is completely free from genuine tannin. This is a matter of considerable importance, in view of the effects of ordinary tea upon the digestion.

It has also been shown that maté contains an appreciable amount of a natural yellow plant colouring matter; it is reasonably certain that this colouring matter is a derivative of flavone.

Certain evidence has been obtained pointing to the presence in maté of caffetannin or some closely allied compound.

Comparisons have been made with coffee and tea, and attention has been drawn to important differences and similarities.

We wish to express our thanks to Dr. C. A. Mitchell and Dr. H. E. Cox for their help and for many useful suggestions received during the course of the work. Thanks are also due to Dr. M. Nierenstein and Mr. Alan Ware for confirming certain results, and to Prof. O. L. V. de Wesselow, Director of the Medical Unit Laboratory, St. Thomas's Hospital, for kindly providing facilities for the work to be done.

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DISCUSSION

Dr. H. E. Cox congratulated the authors on adding so valuable a chapter to the study of maté. He drew attention to Capt. T. A. Joyce's lecture on maté (*Nature*, 1934, **134**, 724), from which it appeared, among much interesting matter, that the first chapter had been written in 1617 by Cornejo, and now Mr. Woodard and his colleague had added one more. It was particularly important to note that the authors had established the absence of true tannin, as in commercial circles it was still asserted that about 7 per cent. of tannin was present. He thought it was a matter for congratulation that the authors had established the nature of the chlorogenic acid and the absence of tannins by definite chemical study, and had not depended solely on colour reactions which were known to be somewhat erratic. It was significant that the hydrolysis yielded caffeic acid, which was known to be a product of caffetannin, and he hoped that they would succeed in establishing the identity of the hydrolysis products of the chlorogenic acid, and also that they would continue their good work, so that we might get to know something of the real constitution of the substances present.

Mr. **Woodard** replied that they had been able to produce quinic acid on distillation with sulphuric acid. They had also been able to show that caffeic acid was present.

Dr. C. A. **Mitchell** said that the authors had made a valuable addition to the long series of papers that had been brought before the Society by way of the Analytical Investigation Scheme. When considering the conflicting statements upon the presence or absence of tannin in products such as maté, it was necessary to have a clear conception of what was meant by "tannin." Definitions for tannin were notoriously vague, but it seemed reasonable to regard a tannin as a substance that would "tan," and for this reason great importance attached to the results of the goldbeaters' skin test, which was essentially a "tanning" reaction. If this test gave negative results, as it did with maté, there could be no true tannin present, but it would be interesting to learn whether the authors had ascertained the nature of the substances that were adsorbed from the extract of maté by hide-powder. In view of the results obtained with goldbeaters' skin, they were evidently not tannins.

Mr. R. L. **Collett** asked whether the green colour obtained with ammonia was also obtained with other alkalis.

Mr. **Woodard**, replying, said that he very much appreciated the remarks made by Dr. Cox. In the first place he would like to emphasise the fact that the work dealt primarily with the question of genuine tannin in maté, and that most of the time at their disposal had been devoted to this purpose. Also, he was of opinion that before any useful knowledge bearing on the chemistry of the plant phenols in maté could be gained, it would be necessary first to separate colouring matter from essential plant phenols and then to purify the products so obtained. This was not an easy matter, although he was pleased to say that reasonable success had been attained in making a separation of the two phenols, and some evidence was given in support of their chemical identity. The green colour given by maté extracts with ammonia was also obtained with solutions of sodium and potassium hydroxide, although the colour was much less intense. He had observed that the green colour was destroyed by acids alone, as well as by reduction with zinc and hydrochloric acid. With regard to the points raised by Dr. Mitchell, he had not considered it necessary to make a full investigation of the substances adsorbed by hide-powder. Since all tests for genuine tannin gave negative results with maté, and also since hide-powder was known to adsorb both colouring matter and non-volatile organic acids, he considered the adsorption in this case to be due to the presence of one or both of these constituents in the leaves. The green colour given by alkalis with aqueous maté extracts was similar in many respects to the bluish-green colour given by coffee extracts under identical conditions. This reaction was commonly attributed to viridic acid, but he thought that this conclusion was a little too hasty. Viridic acid was a substance of unknown constitution, since, according to Vlaaderen and Nhulder (*J. prakt. Chem.*, 1858, **67**, 261), there were at least six different kinds of viridic acid in coffee beans. His own observations led him to regard this interesting colour reaction as an indication of the presence of caffetannin or some closely allied compound.

The Hortvet Freezing-point Process for the Examination of Milk: Correction Factors and the Influence of Stirring: I

By J. R. STUBBS, M.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, December* 8, 1934)

Introduction

Hortvet, with his collaborators under the scheme adopted by the American Association of Agricultural Chemists, began work in the year 1917 on the problem of evolving an apparatus and a technique for the determination of the freezing-point of milk. He aimed at producing a cryoscope which would be convenient to use and by which results could be rapidly obtained with sufficient accuracy for the purpose of examining milk. Other workers, notably Raoult and Monier-Williams, had described forms of apparatus by which accurate results could be obtained, but their cryoscopes were elaborate and difficult to manipulate, and a considerable expenditure of time was necessary to carry out an observation, thus rendering them quite unsuitable for routine work. The position cannot be better described than in the words of Monier-Williams[1]:—"The use of such comparatively complicated apparatus as that shown on page 8 is quite out of the question except for purposes of research"; and again, "The apparatus that I used was too elaborate for routine work."[2]

Hortvet, on the other hand, remarks, "There does not appear to be any fairly defined uniformity in respect to design and construction of apparatus. . . . In order to satisfy practical requirements an attempt has been made to unify the conditions which have been outlined by giving attention chiefly, first, to the construction of a suitable cryoscope and thermometer; and second, to the method of manipulation. The cryoscope . . . has been designed to serve the purposes under discussion; . . . the application of correction factors may, for all practical purposes, be avoided by means of a carefully standardised method of procedure."[3]

This standardised form of instrument and technique was completed in the year 1921, accepted by the A.O.A.C., and became an official method.[4] It has since been fairly extensively used in this country, and in the year 1933 the Council of the Society of Public Analysts recommended that it should be adopted for the examination of milk.[5] It is interesting to observe, in passing, that both Raoult and Monier-Williams felt the need for a less elaborate form of apparatus which would serve for ordinary purposes, and each produced a simplified design of cryoscope.

Experience seems to show that by the use of the Hortvet apparatus reliable and concordant results can be obtained with a minimum expenditure of time and trouble, and, provided that the technique laid down by the regulations is followed, the results of one observer are comparable with those obtained by others. After a somewhat extensive use of the cryoscope for several years I have no hesitation in saying that the process is as rapid as any other suggested process; indeed, it is probably the speediest of all; it is economical, requiring very little ether; it is much more convenient and agreeable to work than processes in which mixtures of ice and salt are employed as the cooling agent; it is under strict control, and it is possible and usual to obtain concordant results in duplicate experiments both by the same observer and also by different observers; and, finally, the degree of accuracy is more than sufficient for the practical purposes for which the examination of milk is undertaken.

But the process has been criticised in some quarters, particularly by Monier-Williams, who has raised objections both to the type of stirrer and to the method of stirring. Thus there are raised the questions whether the results obtained by the use of the Hortvet process will be affected materially by varying rates of manipulation of the Hortvet stirrer, and whether the use of a more efficient stirrer will cause differences in the results; if so, what will be the extent of the variations? The work described in the first part of this paper was undertaken with the object of answering these questions.

It has also been stated, both in the literature and during discussions I have had with other workers, that the Hortvet apparatus and technique do not give a figure from which there can be readily ascertained the "true" freezing-point of milk, *i.e.* the temperature at which milk and ice are in equilibrium with each other, so that the quantity of ice remains constant in amount; that it is difficult, if not impossible, with the standard Hortvet apparatus to arrive at the corrections which should be applied to the observed or apparent freezing-point, on account of supercooling and of heat transference while the temperature is rising after crystallisation begins. These points are dealt with in the second part of this paper.

The apparatus used in all this work was the modified Hortvet cryoscope, referred to in a previous paper,[6] and explained in the second part of the present paper. For the experiments, recorded in the first part of the paper, to ascertain the influence of stirring, the alcohol was retained, as is the case in the usual method of working with the standard Hortvet cryoscope. Unless otherwise stated, stirring was in all cases effected by means of an electric motor causing the stirrer to work at the rate of 40 complete strokes (each stroke consisting of an up-and-down movement) in a minute.

The thermometer used throughout the first series of experiments recorded in the first and second parts of the paper was an American one, which still continues to be very satisfactory after being in use for about three years. It is the one whose good performance is referred to in the paper mentioned above and, as there stated, its indications of the freezing-point of water appear to be nearly independent of any influence, excepting variations in the barometric pressure. The readings were taken with a small hand-lens by which the graduations are in focus when the distance between the lens and the thermometer is about 44 mm. from the thermometer.

The bulk of the work was repeated after a lapse of about three months, when the readings of the thermometer were observed by means of the telescope of a cathetometer. The instrument was clamped to a heavy table, which in turn was screwed to the floor. Two spirit levels were attached to the frame and one to the telescope for the purpose of adjustment. The distance between the end of the telescope and the thermometer was twenty-two inches. The thermometer was adjusted to the vertical position by two plumb lines attached to a movable arm by means of which they could be removed when not required. After a reading had been taken the position of the thermometer was checked, to ascertain if tapping had displaced it from the vertical position.

The time required to make a reading with this levelled telescope is very little, if any, longer than that needed when a hand-lens is used. While the cooling of the milk is taking place the instrument and telescope are levelled and the cross-wires of the telescope brought to bear on the thermometer at about the expected position of the mercury at the freezing-point.

Three readings were usually taken with both the telescope and the hand-lens, and it was found that there was no appreciable difference between readings of the same position of the mercury by the two methods. Experience showed that, after adequate practice, the hand lens gave readings sufficiently accurate for all practical purposes.

Another thermometer, also of American manufacture, which has proved very satisfactory for some months, was used for the purpose of repeating the work.

The zero-point of the thermometer was checked frequently, at least once each working day.

The samples of milk used in all the following work were of good quality as judged by the chemical analysis, and their smell and acidity indicated that they were quite fresh. The temperature of the cooling-bath was maintained at −3·0° C. throughout all the experiments on milk, except in one instance mentioned later; in the case of water, a temperature of − 2·5° C. was used.

PART I

INVESTIGATION OF THE EFFECT OF DIFFERENT METHODS OF STIRRING

(1) *Comparison of the use of the Hortvet stirrer with that of a flat and more efficient one.*

The Hortvet stirrer is described in the *Methods of Analysis of the A.O.A.C.* (3rd Edition, p. 220) as composed of non-corrodible low-conductivity metal . . . the lower end provided with a horizontal loop. It is essentially a length of wire having a loop at right angles at one end, whilst the other end is provided with a handle of insulating material.

This stirrer is to be used with a steady up-and-down motion at the rate of approximately one stroke in one or two seconds. When the desired amount of super-cooling has been obtained, freezing is induced and the thermometer indicates a rise of temperature. The instructions are that, when the freezing-point of water is being ascertained, the stirrer should be manipulated slowly and carefully three or four times as the mercury approaches its highest point. In the case of milk, the stirrer is to be similarly used two or three times at the corresponding point. In effect, then, when the instructions are followed the stirrer is at rest from the moment when freezing begins until the column of mercury "approaches" its highest point.

It will be obvious that, within reasonable limits, it can be of little consequence what rate of stirring is adopted while cooling is taking place, provided that it is effective in mixing the liquid in the freezing-tube so that the temperature indicated by the thermometer is the same as that of the different parts of the liquid; it might be expected that an increase in the rate of stirring would have the effect of reducing the time needed for cooling, in spite of the slight amount of extra heat generated by the more vigorous agitation, and that a reduction in that rate would produce the opposite effect.

It would appear that, in the Hortvet process, the question of stirring, while the temperature is rising after freezing has begun, might assume greater significance, for the final temperature attained is the resultant of at least two opposing effects, *viz.* the abstraction of heat from the freezing liquid by the cooling-bath and the addition of heat due to the latent heat of formation of ice. Vigorous stirring might be expected, by exposing fresh layers of the liquid under examination to the walls of the freezing-vessel, themselves cooled by the cooling-bath, to promote extraction of heat while, at the same time, increasing the rate at which the liquid is heated up by bringing the particles of ice more quickly into contact with the different parts of the liquid.

It must be admitted that the procedure as regards the use of the stirrer in the Hortvet technique during the period now under consideration stands alone and in distinct contrast with that adopted by most prominent observers. Raoult, when examining dilute solutions, used a large platinum stirrer, fitted with two helical vanes, which was fixed over the bulb of the thermometer, and both stirrer and thermometer were rotated together at the rate of 300 revolutions per minute. Monier-Williams, in the experiments recorded in his work published in the year 1914, employed a glass spiral stirrer rotating at a speed of 1300 revolutions per minute, while in his later experiments in 1933 he used an up-and-down flat or disc stirrer manipulated at the rate of one up-and-down stroke every two or three seconds.

From a consideration of the above it will be quite clear that no claim can be put forward that, in the Hortvet process, the mixing together of the ice and the liquid will bear comparison, as regards thoroughness and speed, with that adopted in the technique of Raoult and of Monier-Williams. This point, indeed, would appear so obvious that it can hardly have escaped the notice of Hortvet and his collaborators; it seems reasonable, on the other hand, to presume that vigorous stirring was intentionally avoided.

Monier-Williams definitely suggests that the stirring in the Hortvet method of procedure is "weak," and in his later design of apparatus he himself uses, as mentioned above, a flat stirrer which may be described as a disc with a central hole for the thermometer and two smaller holes, in place of the ring of wire used by Hortvet. Moreover, Monier-Williams directs that this more efficient stirrer should be operated at the rate of one stroke (1 up-and-down motion) in two or three seconds all the time the temperature is rising until the tapping of the thermometer is carried out. So that Monier-Williams not only uses a more efficient stirrer, but also uses it continuously.

For the following experiments there was employed a stirrer, made of thin sheet brass, fastened to one end of the stem of a Hortvet stirrer in place of the ring of wire. The metal disc was 0·7 mm. in thickness and 29·5 mm. in diameter, with a central hole 12·5 mm. in diameter and two small holes, each 4 mm. in diameter, opposite to each other. When this was substituted for the ordinary Hortvet stirrer it was quite obvious, in manipulating it, that a much more vigorous and thorough stirring was obtained; this was proved by the effort needed to work it, and also by the appearance of the milk, which was agitated to such an extent that it was inclined to froth.

In the experiments, the results of which are given in Table I, a comparison was made between the effect of the use of the Hortvet stirrer and the disc stirrer described above. The same portion of milk was used for an experiment with both types of stirrer; in the first experiment the Hortvet stirrer was used first, followed by the flat one; in the second, this order of use was reversed, and so on alternately. Supercooling was carried out to approximately the same extent in every case, and never differed by more than 0·02° for the experiments on the same milk.

In those cases where the Hortvet technique was used no stirring at all was done while the mercury was rising, until it was approaching the highest point, when three up-and-down strokes were slowly made just previous to tapping. Where the flat or disc stirrer was employed, stirring was carried out all the time the temperature was rising from the lowest to the highest point, and at the rate of one complete (1 up- and 1 down-movement) in 2 seconds. This manipulation was done by hand and carefully timed.

The cooling of the milk in the freezing-vessel was much more rapid when the disc stirrer was used than when the Hortvet stirrer was employed. It was found also that when the flat stirrer was used, spontaneous freezing, *i.e.* freezing without the introduction of a particle of ice, took place rather frequently, rendering, sometimes, several attempts necessary before the desired amount of supercooling could be obtained. This never happened in those instances where the Hortvet stirrer was used. The freezing-point of water was taken with each of the two methods of stirring, and identical readings were obtained.

The results of the experiments are given in Table I.

TABLE I

Effect of different methods of stirring

No. of sample	Hortvet stirrer Δ*	Flat stirrer Δ
Reading by hand-lens		
20863 L.B.D.	0·552	0·552
20867 L.B.D.	0·553	0·553
83583 Ws.D.	0·541	0·541
83589 Ws.D.	0·548	0·546
93438 Wgn.D.	0·533	0·533
53477 R.D.	0·541	0·541
Reading by levelled telescope		
53562 R.D.	0·546	0·548
83665 Ws.D.	0·550	0·551
83668 Ws.D.	0·550	0·548
76548 S.D.	0·538	0·538
76552 S.D.	0·548	0·548
76554 S.D.	0·539	0·539

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* Δ is the depression of the freezing-point of milk below that of water, the reading of the thermometer being corrected for zero-point and irregularities of bore. It is of the same numerical value as the freezing-point, but opposite in sign.

It will be seen from the above table that in eight cases identical results were obtained by the use of the two different stirrers, and that in the remaining cases small variations of not more than 0·002° were obtained.

This result was unexpected. The explanation may be that the flat, efficient stirrer used as described, distributes quickly through the liquid the heat liberated on the formation of ice, but, at the same time, the thorough stirring of the liquid increases the rate at which heat is abstracted from the contents of the freezing-tube. On the other hand, when the Hortvet stirrer and technique are used, the particles of ice and liquid are not so quickly and thoroughly brought into contact with each other, causing the heating-up to take place more slowly, but the comparatively quiescent state of the outer layers of liquid nearest the cooling-bath hinders the process of abstraction of heat, causing the resultant to be about the same in both cases. Another factor, the accession of heat from the atmosphere, is probably not very different, whichever method of stirring is employed, and contributes its quota to both in much the same amount.

There is one distinct difference which was invariably observed in the experiments described above. In the cases where the Hortvet stirrer was employed, the time occupied by the mercury of the thermometer in rising from the lowest to nearly the highest point was definitely greater than the corresponding period when the efficient stirrer was used. This time, measured by means of a stop-watch from the onset of freezing until tapping was carried out, was, in the case of the Hortvet technique, about 90 seconds, and, with the flat stirrer, about 30 seconds; that is, about three times as long in the one case as in the other. The obvious explanation of this would appear to be that vigorous stirring, by exposing quickly fresh surfaces of ice and liquid to each other, increases the rate of heating, while the comparative slowness with which mixture must take place where there is practically no stirring has the opposite effect.

Monier-Williams[6] suggests that "in the Hortvet apparatus steadiness of temperature at the freezing-point is secured by a fortunate oversight in the matter of stirring." But may it not be that Hortvet has made an attempt, more or less successful, if the above experiments are taken as an indication, to diminish the action of the cooling-bath during the time freezing is in operation without the removal of the alcohol from the jacket surrounding the freezing-tube, and so to arrange matters that the mercury column remains constant at the observed freezing-point sufficiently long to enable several tappings and readings to be made? It is suggested that he may have intentionally avoided energetic stirring, in order to secure a longer period of rest of the mercury than would otherwise have been the case. There can be no doubt that he aspired to produce an apparatus which would be capable of giving results with a minimum of manipulation, and one which would, therefore, be suitable for routine use.

If, in the process, the alcohol need not be removed and a satisfactory result can still be obtained for the freezing-point, it is a very definite recommendation for the adoption of non-removal in a routine process. The reduction in the amount of manipulation and the saving of time, consequent on the non-removal of alcohol, will be acknowledged, it is confidently thought, by all who have had experience of the two methods when undertaking the examination of a number of milks.

There was nothing in these experiments to warrant any suggestion that the use of a flat efficient stirrer would be preferable to that of the standard Hortvet pattern used according to the Hortvet technique with, possibly, the slight variation suggested below.

(2) *The Hortvet stirrer—comparison between its use as prescribed in the A.O.A.C. regulations and its continuous use.*

In this series of experiments I employed the Hortvet stirrer throughout, comparing the effects of using it as prescribed in the A.O.A.C. regulations and also continuously, while warming-up by means of the latent heat of formation of ice was in progress. It has been shown that vigorous stirring and practically no stirring gave the same, or nearly the same, readings for the freezing-point but, since two different types of stirrers were used, there still remained the question if, when using the Hortvet stirrer, different rates of manipulation would affect the results.

There appeared, too, to be another reason which would justify the carrying out of this comparison. It was noticed during the work described in the previous section that the rate at which the mercury "approached" the highest point, as judged by the use of a hand-lens, after freezing had been induced, was at first rapid and then gradually became slower and slower, especially when the Hortvet technique was being followed, and that the last 0·035° in that case took about 45 seconds, compared with the whole time of rising of about 90 seconds—that is, half the period was taken by the last 0·035°. The watching for the highest point reached is, therefore, apt to become tedious, and some considerable practice is desirable because the column rises so slowly. It might be an advantage if this time could be shortened, which, it was thought, might possibly happen if stirring were resorted to during the time the temperature was rising. It was therefore decided to carry out the work described below, comparing the effects of continuous stirring with those of the procedure laid down in the Hortvet technique.

Both varieties of stirring were practised on the same quantity of milk, the sequence of the two methods being alternated in consecutive experiments. The supercooling was practically the same in every case; the greatest difference in the experiments on any one milk did not exceed 0·02°. Table II gives the results. The freezing-point of water was taken with the two methods of stirring, and identical readings were obtained.

It will be seen from this table (p. 154) that the results are in close agreement, and in no case differ by more than 0·002°, an amount so small that it cannot be regarded as significant.

There was observed, however, as in the case where two different types of stirrers were used, a difference in the time required by the mercury column to rise, after freezing had begun, to nearly the highest point, when tapping was needed. With the Hortvet method this period is about 90 seconds, and, with continuous stirring, roughly 60 seconds, and, for the last 0·035° or so, about 45 and 21 seconds respectively. Although the difference between the two latter figures is only 24 seconds, it is very noticeable in working, and the shorter time is a distinct advantage in judging the attainment of the nearly stationary position. It might,

TABLE II

Comparison of the effect of different methods of using the Hortvet stirrer

No. of sample	Hortvet's method Δ	Continuous stirring Δ
Reading by hand-lens		
53479 R.D.	0·535	0·536
25321 H.B.D.	0·535	0·537
960 Westhoughton	0·542	0·542
970 ,,	0·547	0·547
973 ,,	0·536	0·537
30669 C.D.	0·550	0·551
Reading by levelled telescope		
76547 S.D.	0·540	0·542
76549 S.D.	0·539	0·539
76550 S.D.	0·539	0·537
25428 H.B.D.	0·543	0·542
25430 H.B.D.	0·532	0·532
25433 H.B.D.	0·541	0·539

therefore, be worthy of consideration whether the Hortvet technique should be altered so as to permit of a certain amount of stirring during the ascent of the mercury column.

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PARTS II AND III TO FOLLOW.

Tests for Elements in Organic Compounds

BY H. MIDDLETON, M.Sc., A.I.C.

SINCE the use of an alkali metal (Laissaigne's method), or of Castellana's mixture of magnesium powder and anhydrous potassium carbonate, is attended with certain disadvantages and some danger, the following substitutes are proposed:

I. *An intimate mixture of pure anhydrous sodium carbonate and one-tenth of its weight of pure sucrose.*

An ignition tube, about 2¼″ long, made from ordinary glass tubing, ¼″ outside diameter, with a bulb slightly wider than the stem, is suitable for the test.

If the organic substance is a solid, an amount roughly twice the bulk of a rice grain is mixed with about 5 times its bulk of the reagent; the mixture is then introduced into the bulb of the tube and the reagent is added until, after tapping down, there is a column about 1″ long above the bulb.

For a liquid, two or three drops are introduced into the bulb, and the reagent is added until, after tapping down, the column extends to within about ½" of the mouth of the tube.

The tube is now held horizontally and heated in a flame about 2½" high, at first just above the mixture, in order to prevent movement of the latter along the tube. The column of mixture is then gradually heated to redness, the tube being turned over periodically to prevent undue bending. When a portion of the column equal in width to the flame has been heated, the tube is held at an angle, so that while this portion still remains in the flame the heating is gradually extended until the bulb as well as the stem is in the flame.

The idea is to heat the organic substance very gradually by bringing it nearer and nearer to the flame, any vapours evolved passing through the red-hot column of mixture.

Finally, the whole tube is heated to redness in a large flame for a minute or more and then plunged into about 10 ml. of distilled water in a porcelain dish. The contents of the dish are then heated to boiling, and filtered.

As when sodium is employed, halogens are converted into sodium halides, sulphur into sodium sulphide, and nitrogen (in a limited number of cases) into sodium cyanide.

The proportion of sugar employed does not cause excessive fumes when the mixture is heated, yet provides sufficient carbon for the reduction of sulphates, etc., to sulphide. The final heating to redness is essential, in order to cause any such reduction, to decompose the sugar thoroughly, and to remove any deposit from the mouth of the tube, so that a perfectly colourless filtrate is obtained.

Tests for sulphur, nitrogen, and halogens are carried out with the alkaline filtrate as in Laissaigne's method, except that in the nitrogen test a few drops of aqueous sodium hydroxide solution are added before the ferrous sulphate.

RESULTS WITH THE ALKALI-SUGAR TEST.—(*a*) *The test for sulphur.*—A brown or black precipitate on the addition of one drop of lead acetate solution to about 1 ml. of the alkaline filtrate has been obtained with 50 compounds, representing the following classes:

Sulphates of bases, alkyl sulphates, bisulphite compounds, thioureas, thiocyanates and isothiocyanates, sulphones, sulphonic acids and their salts, chlorides, esters, amides and substituted amides, derivatives of phenthiazine and thioindigo.

(*b*) *The test for nitrogen.*—A deep blue solution or precipitate was obtained with only a limited number of compounds, which included the following:

p-Nitrotoluene, *m*-dinitrobenzene, 2 : 4-dinitrotoluene, trinitrotoluene, *o*-nitrochlorbenzene, 2 : 4-dinitrochlorbenzene, uric acid, caffeine, theobromine, theophyllin, barbitone, phenylbarbitone, urea and its nitrate, hydrochloride, and oxalate, ethyl urethane, oxamide, succinamide, chloralformamide, thiourea, glycine, hippuric acid, hexamine, ethyl cyanacetate, acetone semicarbazone, antipyrine and amidopyrine.

With a number of other compounds a green solution was obtained, which, since a blank test with the mixture gave a solution of pure yellow colour (*i.e.* the colour of ferric chloride acidified with hydrochloric acid), is a sufficient indication of the presence of nitrogen in the organic compound.

If a negative or doubtful result is obtained, the alkali-zinc test (II) must be tried.

With the exception of thiourea, poor or negative results were obtained with substances which contain sulphur in addition to nitrogen.

Negative results were usually obtained with aromatic bases, and their salts and derivatives.

If a negative result is obtained (although the subsequent alkali-zinc test proves the presence of nitrogen), there is the compensating advantage that the alkaline filtrate to be tested for halogens contains no cyanide.

(*c*) *The tests for halogens.*—The usual tests with the alkaline filtrate have been carried out, with highly successful results, with 40 chloro-compounds, 15 bromo-compounds, and 6 iodo-compounds, exclusive of salts of bases with the halogen acids.

II. *An intimate mixture of zinc dust and half its weight of anhydrous sodium carbonate (ordinary commercial products).*

This mixture is employed only if a negative result for nitrogen has been obtained in the alkali-sugar test.

The test is carried out in exactly the same way as when the alkali-sugar mixture is used. The gradual heating is particularly necessary in this case, as otherwise negative results may be obtained with salts and derivatives of aromatic bases.

Nitrogen only is tested for in the alkaline filtrate.

RESULTS WITH THE ALKALI-ZINC TEST FOR NITROGEN.—The results obtained with 220 compounds varied from dense blue precipitates to blue-green solutions, yielding a blue residue after boiling (to coagulate the precipitate), cooling and filtering.

The substances tested represent the following classes:—Ammonium salts, amides, urea and its salts, aryl substituted ureas, urethanes, ureides, purine group, nitriles, thiocyanates and isothiocyanates, compounds of aldehydes with ammonia, oximes, phenylhydrazones and semicarbazones, esters of nitric and nitrous acids, amino-compounds and their salts, acetyl, benzoyl, benzylidene and *p*-toluene sulphonyl derivatives, aromatic and heterocyclic secondary and tertiary bases, nitro-, azo-, and diazo-amino compounds, picrates of organic compounds, simple and substituted sulphonamides, alkaloids, derivatives of pyrazolone, indigo and indanthrene.

The alkali-zinc mixture, with constituents of A.R. quality, may also be used for sulphur and halogens, provided that the tests for chlorine and sulphur are made in comparison with a blank test.

The test for sulphur is carried out as follows:—After the hot tube has been plunged into water, the mixture is heated to boiling and allowed to settle, and the liquid is then decanted through a filter. To the residue in the dish (containing insoluble zinc sulphide if sulphur is present in the organic compound) are added about 10 ml. of dilute hydrochloric acid, and a filter paper (upon the centre of which a drop of sodium plumbite solution has been poured) is immediately placed over the dish.

If sulphur is present in the organic compound, a dark brown stain, visible on the upper surface of the paper, will be formed.

Blank tests gave only a slight brown stain, visible only on the under surface of the paper.

The alkali-sugar test appears preferable, however, since the constituents of the mixture can be obtained quite free from chlorine and sulphur; moreover, the test for sulphur is simpler, and involves less time.

ADVANTAGES OF THE ALKALI-SUGAR AND ALKALI-ZINC MIXTURES.—(i) The mixtures are readily prepared (it is not necessary to dry the sodium carbonate) and convenient to handle, and may be kept without any special precautions.

(ii) The tests are applicable without modification to very volatile substances, *e.g.* ethyl bromide (b.p. 38° C.).

(iii) Except in the case of picric acid and picrates of organic compounds the reactions are perfectly quiet, even with nitrates and polynitro compounds.

With picric acid and picrates, the mixture, or a portion of it, is harmlessly ejected from the tube, this behaviour affording an indication of this class of compound.

In the event of the tube bursting there is no startling flash, as is the case with the magnesium mixture.

(iv) The plunging of the hot tube into water is attended with less danger, or with less startling results, than when an alkali-metal or the magnesium mixture is used.

(v) No cyanide is formed when either mixture is heated alone. When the magnesium mixture in the recommended proportions of 1 part of magnesium to 2 parts of potassium carbonate is strongly heated alone, under the conditions essential for carrying out the test with a very volatile substance, *i.e.* in an ignition tube, sufficient cyanide is formed to give a dense blue precipitate when the nitrogen test is applied. Apparently, atmospheric nitrogen plays a part in the reactions.

When the proportions of 3 parts of magnesium to 1 part of potassium carbonate are employed, however, only a slightly green solution is obtained.

(vi) The alkali-zinc test has the great advantage over all other methods, that the test for nitrogen is not interfered with by the presence of sulphur in the organic compound.

On applying the test to 30 substances containing sulphur in addition to nitrogen, no sulphide or thiocyanate was detected in the alkaline filtrate containing the cyanide.

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The Specific Gravity of Fatty Oils Shipped in Bulk

By E. R. BOLTON, F.I.C., M.I.Chem.E., and K. A. WILLIAMS, B.Sc., F.I.C.

In cases where the specific gravity or density of an oil is required to be determined with great accuracy at a given temperature, the measurement must obviously be made at that temperature. In practice, however, it is customary to make the determination at some neighbouring temperature and to calculate the required specific gravity or density from the figure so obtained by the use of a correction. The usual correction is derived from the experimentally-determined fact that an alteration of 1° C. in temperature causes a change in specific gravity of 0·00069 in the case of most, if not all, liquid oils.

This method has certain practical advantages, and works very well so long as it is applied only to liquid oils. Unfortunately it has also been the custom to proceed in a similar manner with semi-solid fats and oils which contain stearine at normal temperatures; the determinations are made at a raised temperature with the oil completely liquid, and "specific gravity" at 15·5° C., or other lower temperature, is calculated by means of the above correction. This leads to gross inaccuracies, as the correction is valid only for liquid oils and becomes modified as soon as stearine crystallises and solidification begins. The true correction varies and depends on the proportion and nature of the stearine present.

We have obtained the following values for a few of the corrections to illustrate this:

Sardine oil	0·00080 to 0·00105
Pilchard oil	0·00090 (approx.)
Palm oil	0·00140
Crude sperm oil	0·00187

It will be seen that these figures vary up to nearly three times the conventional figure. In a recent case which came to our notice the specific gravity of an oil had been returned as 0·880 instead of the correct figure of 0·894, solely because the wrong correction had been employed.

A further difficulty arises because stearine is much denser in the solid than in the liquid form and crystallises slowly from oils, with the result that supercooling without crystallisation may occur. It is quite possible to have an oil at a given temperature in a liquid state or in varying degrees of solidification. The specific gravity of each is quite different, as is exemplified in the following table, all the figures in which were obtained on a normal palm oil at 32·5° C.

Specific gravity of a palm oil at 32·5° C./15·5° C.

Condition of oil	Observed specific gravity
Liquid	0·9006
Some stearine present	0·9025
Semi-solid	0·9050
Solid	0·9084

The shipment of very large tonnages of oil in bulk is becoming more and more popular, and many problems have arisen in connection therewith. Among these, perhaps, the most important concern the determination of the weight of oil in a ship's tank or in the shore-tank into which it is discharged.

This weight is obtained by calculation from the volume occupied by the oil in the tank at a known temperature, and an accurate specific gravity or density of the oil determined at the same temperature. It is necessary also to know the condition of the oil (*e.g.* partly solid and partly liquid) when its volume is measured.

As has been previously pointed out (E. R. Bolton, "Oils, Fats and Fatty Foods," 1928, p. 33, and A. Torisawa, "Bulk Oil," 1929, p. 47), the factor required for converting the volumes to weights depends on the units in which they are expressed. In Great Britain it is based on the statutory relations between gallons and pounds, and for practical purposes is the ordinary *specific gravity*, in which the weight of a given volume obtained at the required temperature in air is compared with the weight of an equal volume of water obtained at 15·5° C. in air. On the Continent the weight is required in kilograms, although it may be subsequently converted into tons by a conventional factor (1 ton = 1016 kg.). The volume is measured in litres, and the factor required is a *density—viz.* the weight (in air) in kilograms of one litre of oil measured at the required temperature. The reference standard is the weight *in vacuo* of a standard volume of water measured at 4° C.

The difference between the specific gravity and the density figures for a given oil amounts to about 0·2 per cent.

Five thousand tons of palm oil is a quantity commonly dealt with in a bulk shipment, and with such a quantity the difference between the extreme figures shown in the above table would involve an error of about 43 tons in the apparent out-turn; and with palm oil at £17 per ton this would involve a sum of £731.

In most cases the specific gravity or density required is that of the oil when it contains the maximum amount of stearine (*i.e.* during cold weather). In order to obtain this figure it is most satisfactory to fill the specific gravity bottle with oil in a liquid condition, cool it to a temperature some 5 to 8 degrees below that at which the determination is required, and keep it at that temperature until as much stearine as possible has separated (usually this requires 24 hours). Precautions should be taken to see that no air is sucked into the mass of oil during crystallisation. After allowing it to stand in this manner, the stopper is inserted and the bottle and its contents are warmed to the required temperature in a thermostat until expansion ceases; the stopper is then wiped and the outside of the bottle cleaned as usual; the weight of the bottle and contents is obtained after it has attained the room temperature.

This method has now been adopted by many leading authorities, and is not claimed to have any novel features; but we feel that it is desirable that it should receive wide attention, as disputes continually arise about specific gravities and densities, and we find, almost always, that they are due to a lack of understanding of the facts we have mentioned above.

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Preliminary Notes on the Sterol Iodine Values of Oils and Fats by the Bolton and Williams Method

By A. C. BOSE, Ph.D., A.I.C.

In the present investigation an attempt has been made to determine the sterol iodine values (S.I.V.) of various oils and fats of authentic origin by the method of Bolton and Williams. In addition to samples of the oils and fats of known purity included in each of the four groups by Bolton and Williams in Table I[1], a few samples of other oils in common use in India have also been analysed.

The objects of the investigation were to corroborate for Indian oils the Bolton and Williams values, and to ascertain whether the method can be used for detecting and estimating the degree of adulteration of oils and fats in one group with those of the other groups, with special reference to olive oil.

Although the method of Bolton and Williams affords the means of classifying oils and fats of both animal and vegetable origin, yet I have found that with some Indian samples the sterol iodine values do not fall exactly within any of the four specified groups, but occupy intermediate positions between them. (*Cf.* Table I.)

In the process of extraction of oils from different varieties of mustard, rape and similar oil-seeds, niger-seed (surgônja) is generally added as an adulterant, since, being harder, it helps to increase the yield of the extracted oil. It is thus obvious that, since the sterol iodine value of niger-seed oil is fairly close to those of the mustard oils (*cf.* Tables I and II), it would be difficult to employ the Bolton and Williams method to detect or estimate the percentage of adulteration in them. It is also evident from Table II that there is no correlation between the sterol iodine value and the butyro-refractometer reading or saponification value of oils and fats.

The usual adulterants of ghee are hydrogenated vegetable oils, coconut oil, rapeseed oil, and almond and similar edible oils. During the winter in tropical countries ghee can be readily adulterated with coconut oil, which solidifies with the ghee on cooling, whereas other edible oils which do not solidify can be used as adulterants only during the summer.

The estimation, or even detection, of such adulterants as occur in Group I by this method is obviously impossible, because the sterol iodine values of such mixtures will be of the same order after adulteration of the ghee, in any proportion, with any of the oils of the first group.

An authentic sample of "vanashpati," which consists of a mixture of hydrogenated vegetable oils, was analysed. It had the appearance of ghee, and gave a sterol iodine value of 93·5, which is characteristic of oils in Group II. A mixture in equal proportions of "vanashpati"* and ghee was also analysed. The analytical results show that easy detection and approximate estimation of adulterants that occur in groups other than the first may be effected, provided that the sterol iodine value of the actual adulterant is known. (*Cf.* Table III and the example.)

A sample of cow-ghee prepared in the laboratory was separated, by ordinary filtration, into a solid and a liquid fraction at a temperature of about 30° C., and the physical properties of the two fractions were examined. The liquid fraction gave higher values for all the constants determined.

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*An Indian name for vegetable ghee.—Editor.

The sterol iodine value of cow-ghee, on storage, appears to diminish, whilst the saponification value remains nearly the same. (*Cf.* Table IV.) Judging by the results given by two samples, there appears to be a relationship between the sterol iodine value and the Reichert–Wollny value; this will be investigated later.

It will be seen from the results in Table IV that the sterol iodine values for old ghee range from 52 to 58. If this range for cow-ghee, or for any other oils or fats, can be confirmed on a large number of samples, it is suggested that such fats should be placed in Group "Zero" with reference to olive oil, so as to take their place in Bolton and Williams Table I.

Detailed work on the sterol iodine values of cow-ghee and buffalo-ghee is in progress.

EXPERIMENTAL.—Two quantities (2·5 g. each) of the oil or fat were hydrolysed for an hour in roomy conical flasks with 25 to 30 ml. of $N/2$ alcoholic potash. The alcohol used for this solution was purified by treatment with silver nitrate and potassium hydroxide and re-distillation; the alcoholic potash made with it remained brilliant and did not develop a yellow tint. After neutralisation (determination of the saponification value), the contents of the flasks were transferred to two separators, and each solution was washed with 50 ml. of water, and then extracted with three successive portions of 50 ml. of ether. The ethereal extracts were washed, gently at first and then vigorously, three times with 20 ml. of water, then three times with $N/2$ potassium hydroxide solution, and again with water in 20-ml. portions until free from alkali. The washed extracts were transferred to small, weighed conical flasks, and the ether was distilled off completely. The residues were treated with 2 to 3 ml. of acetone, which was then evaporated at as low a temperature as practicable, the last traces being drawn off by means of a current of dry air, and the flasks with the residues were dried in an air-oven at 80° C. until constant in weight (about 30 minutes). The unsaponifiable matter was dissolved in 5 ml. of chloroform, the solution was treated with 20 ml. of $N/10$ pyridine sulphate bromide solution and left for exactly 5 minutes, after which it was treated with 5 ml. of 10 per cent. potassium iodide solution and 40 ml. of water, and titrated with $N/20$ sodium thiosulphate solution.

A blank determination was made simultaneously, and the strength of the sodium thiosulphate solution was determined against $N/10$ potassium dichromate solution.

All the figures given in the following tables below have been verified by duplicate, and in some instances, four determinations.

TABLE I

Sample	Butyro-refractometer reading	Iodine value (Wijs)	Saponification value	Unsaponifiable matter Per Cent.	Sterol iodine value	Group
Poppy-seed oil	67·0	—	196·0	0·644	82·15	I–II
Niger-seed oil (surgônja)	63·0	132·1	190·4	0·964	109·30	II–III
Pila Sarso (yellow mustard) oil	58·6	101·8	172·5	0·960	130·97	III–IV

TABLE II

Sample	Butyro-refracto-meter reading	Iodine value	Saponifi-cation value	Unsaponi-fiable matter Per Cent.	Sterol iodine value	Group
Cocogem	34·6	—	255·0	0·276	70·2	I
Coconut oil	34·6	—	258·7	0·296	67·4	I
Vanashpati	51·0	—	188·7	0·460	93·8	II
Linseed oil	72·8	177·0	189·8	0·920	122·8	III
Tori-seed oil (mustard)	59·0	101·1	173·6	0·890	117·5	III
Mixed mustard oil ..	59·0	101·4	173·0	0·970	121·5	III
Arachis oil	55·5	93·8	187·0	0·520	117·3	III
Castor oil	68·6	—	180·3	0·490	125·0	III
Cod-liver oil*	68·5	—	184·8	0·940	100·4	II–III

* Obtained from a medical store.

TABLE III

Sample	Butyro-refracto-meter reading	Reichert–Wollny value	Saponi-cation value	Unsaponi-fiable matter Per Cent.	Sterol iodine value	Group
Ghee (A)	40·5	38·2	235·8	0·42	63·2	I
Vanashpati (B)	51·0	0·2	188·7	0·46	93·5	II
(A+B) in 50 per cent. mixture	45·1	—	213·6	0·44	77·8	I–II
Theoretical value [mean of (A) and (B)]	45·8	19·2	212·3	0·44	78·35	I–II

Example: In a mixture of fats and oils, say of "B" with A, *a* is the per cent. of adulterant. If the S.I.V. of the adulterant, B, is known, *a* can be calculated by the equation,

$$\frac{B\times a}{100}+\frac{S(100-a)}{100}=F \quad \ldots \quad \ldots \quad \ldots \quad \ldots \ (1),$$

where B represents the S.I.V. of the adulterant (which must be known); S, the standard S.I.V. for the sample obtained from the Table; and F, the S.I.V. of the mixture (found by actual determination). Then, using the actual data from Table III, we have B = 93·5 (Vanashpati); S = 63·2 (Ghee); F = 77·8 (Mixture A + B) in 50 per cent. Substituting the values in (I), we get

$$\frac{93{\cdot}5\times a}{100}+\frac{63{\cdot}2(100-a)}{100}=77{\cdot}8,\ \text{or}\ a=48{\cdot}2.\quad \text{Percentage error} = -\ 1{\cdot}8.$$

Again, when the data are taken reversely, we get

$$\frac{63{\cdot}2\times a}{100}+\frac{93{\cdot}5(100-a)}{100}=77{\cdot}8,\ \text{or}\ a=51{\cdot}8.\quad \text{Percentage error} = +\ 1{\cdot}8.$$

TABLE IV

Sample	Reichert-Wollny value	Butyro-refractometer reading	Saponification value	Unsaponifiable matter Per Cent.	Sterol iodine value	Group
Ghee A	38·2	40·5	235·8	0·43	63·2	<I
Ghee B (old)	35·1	40·5	234·1	0·49	52·05	<I
Cow-ghee (C) (old) ..	—	41·0	222·5	0·46	58·48	<I
New cow-ghee (C) (solid fraction)	—	42·4	220·6	0·39	60·8	<I
New cow-ghee (C) (liquid fraction)	—	42·7	223·4	0·43	65·4	I

SUMMARY.—The Bolton and Williams values for fats and oils have been corroborated, and those for some new samples of Indian origin have been added.

Adulteration of ghee with such fats and oils as occur in Group I cannot be detected or estimated, whilst adulteration with fats of groups other than the first can be easily detected and approximately estimated, provided that the S.I.V. of the adulterant is known.

I wish to thank the Director of Public Health, Bihar and Orissa, for his kind permission to carry out this investigation in his laboratory.

REFERENCES

1. E. R. Bolton and K. A. Williams, ANALYST, 1930, **55**, 5.
2. "Report of the Sub-Committee on the Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps, to the Standing Committee on Uniformity of Analytical Methods," ANALYST, 1933, **58**, 205.

The Determination of Small Amounts of Sulphur in Certain Organic Compounds

BY N. STRAFFORD, M.Sc., F.I.C., AND H. CROSSLEY, A.M.C.T.

THE determination of small amounts of sulphur in certain dyestuffs intermediates, *e.g.* nitrobenzene, proved to be a matter of some difficulty. As the accurate determination of amounts of sulphur of the order of 0·01 per cent. was called for, it was evidently necessary to provide a method for the decomposition of a considerable quantity of the material under examination, with quantitative recovery of the sulphur.

The possibility of employing "wet" methods, such as oxidation with bromine and nitric acid or with nitric and perchloric acids, or reduction with sodium and amyl alcohol, was explored, but without success.

Attention was next directed to combustion methods. Existing methods for the determination of sulphur in organic liquids by combustion may be classified broadly under (i) the "lamp" method in which the liquid is burned directly from a wick*, and (ii) combustion of the vaporised material in a heated tube. In methods of the latter type the liquid may be vaporised (*a*) from a boat contained in the combustion tube,[1] or (*b*) by passing a current of air through the liquid contained in an auxiliary tube which may be suitably heated.[2]

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* *Cf.* "Standard Methods for Testing Tar and its Products," 1929: Published by Standardisation of Tar Products Test Committee, 166, Piccadilly, London, W.1. Determination of sulphur in light benzol, serial LB 11, p. 90.

The lamp method is not directly applicable to liquids such as nitrobenzene, for, even after dilution of the liquid with five times its volume of alcohol, combustion is not complete, the flame being very smoky.

The existing methods of combustion in a heated tube were found to be inadequate for the determination of traces of sulphur in liquids such as nitrobenzene. Volatilisation of the liquid from a boat in the combustion tube suffers from the defect that only relatively small amounts of the substance can conveniently be handled, and it is, moreover, very difficult to maintain conditions giving regular and complete combustion. Volatilisation from an auxiliary tube, which has been applied with success to a volatile liquid such as benzene[2] fails completely with liquids of higher boiling-point. A modification of the method in which vaporisation was effected by passing air through the nitrobenzene, maintained at or near its boiling-point, gave unsatisfactory results.

Attention was therefore directed to devising an apparatus for the production, at a steady rate, of a correctly proportioned mixture of substance and air. The apparatus ultimately evolved consists essentially of a spraying apparatus of a well-known type in which the spray is produced by a jet of air blown across the orifice of a narrow tube dipping into the liquid. The spray is carried by the air-current into the combustion tube.

In the preliminary experiments the spray was operated by applying a pressure above that of the atmosphere, but it was found later that quite satisfactory spraying with more uniform control was obtained by aspirating by means of a water vacuum-pump.

By this means, rapid, even and complete combustion was realised, the time required for the combustion of 20 g. of nitrobenzene being about 30 minutes. By contrast, in the Davidson lamp method, the (imperfect) combustion of 2 g. of nitrobenzene, diluted with 8 g. of alcohol, takes about 6 hours.

Results Obtained.—Experiments in which the method (described in detail later) was applied to different samples of technical nitrobenzene gave the results shown in Table I.

TABLE I

Determination of sulphur in samples of technical nitrobenzene

Sample	Weight of sample taken g.	Weight of barium sulphate g.	Sulphur found Per Cent.
(*a*)	14·15	0·0857	0·083
	15·00	0·0767	0·070
	18·91	0·1031	0·075
	23·91	0·1329	0·075
(*b*)	14·01	0·0231	0·023
	23·33	0·0339	0·020
(*c*)	12·99	0·0103	0·011
	16·48	0·0131	0·011
	15·04	0·0171	0·016

In a further series of experiments in which to a sample of nitrobenzene were added known quantities of (*a*) carbon disulphide and (*b*) thiophen, the results shown in Tables II and III were obtained:

TABLE II

Determination of sulphur in nitrobenzene with known amounts of carbon disulphide added

(*a*) The nitrobenzene contained 0·013 per cent. of sulphur.

	Weight of sample g.	Weight of barium sulphate g.	Total sulphur found Per Cent.	Sulphur (corrected for S present in nitrobenzene) Per Cent.	Sulphur added Per Cent.	Error
(i)	13·15	0·1853	0·194	0·181	0·207	—0·026
	14·45	0·2198	0·208	0·195	0·207	—0·012
(ii)	14·04	0·1136	0·111	0·098	0·102	—0·004
	12·31	0·1019	0·098	0·100	0·102	—0·002
(iii)	16·30	0·0951	0·080	0·067	0·057	+0·010
	13·71	0·0744	0·074	0·061	0·057	+0·004

(*b*) The nitrobenzene contained 0·011 per cent. of sulphur.

	Weight of sample g.	Weight of barium sulphate g.	Total sulphur found Per Cent.	Sulphur (corrected for S present in nitrobenzene) Per Cent.	Sulphur added Per Cent.	Error
(iv)	15·99	0·1161	0·100	0·089	0·097	—0·008
	14·50	0·1010	0·095	0·084	0·097	—0·013
	14·67	0·0985	0·092	0·081	0·097	—0·016

TABLE III

Determination of sulphur in nitrobenzene with a known amount of thiophen added

The nitrobenzene contained 0·013 per cent. of sulphur.

Weight of sample g.	Weight of barium sulphate g.	Total sulphur found Per Cent.	Sulphur (corrected for sulphur in nitrobenzene) Per Cent.	Sulphur added Per Cent.	Error in sulphur
14·15	0·0660	0·064	0·051	0·057	—0·006
16·49	0·0825	0·068	0·055	0·057	—0·002

The results in the preceding tables show that, when applied to nitrobenzene, the method is capable of giving results accurate to within ± 10 per cent. for sulphur-contents from 0·05 to 0·2 per cent.

Subsequent investigation showed that the method was applicable to a number of other organic substances. With certain hydrocarbons, *e.g.* paraffins, naphthalene, etc., and bodies other than nitro compounds, with a low oxygen-content, it was found necessary to dissolve the sample in about an equal weight of nitrobenzene of known sulphur-content before combustion. Combustion of solid nitro bodies, *e.g.* *p*-nitrotoluene and nitronaphthalene, may be effected either by dissolving the substance in nitrobenzene, or by heating it to a temperature slightly above its melting point and pre-heating the air passed into the spray apparatus.

Satisfactory results have been obtained with the substances shown in Table IV.

TABLE IV

Substance	Sulphur found Per Cent.	Substance	Sulphur found Per Cent.
Benzene	0·016 0·017	α-Nitronaphthalene	0·083 0·082 0·084 0·086
Naphthalene (sample *a*)	0·176 0·177		
Naphthalene (sample *b*)	0·087 0·087	α-Naphthylamine	0·021 0·016
Kerosene	0·036 0·040	Aniline	0·005 0·002
Toluene	0·05 0·04	*o*-Dichlorobenzene	0·23 0·24
Pyridine	0·015 0·014	*p*-Nitrotoluene	0·0081 0·0082
α-Picoline	0·058 0·056	*p*-Chloronitrobenzene	0·003 0·003
		Methyl alcohol*	0·0008

* The weight of methyl alcohol burned was 168 g., the time required being 2 hours 10 minutes.

The method has been employed successfully in an independent laboratory for the determination of small amounts of sulphur in ethyl alcohol.* Some of the results are given in Table V, together with those obtained by a modified lamp-method.

TABLE V

Sample	Lamp method (modified) Sulphur Per Cent.	Combustion (spray) method Sulphur Per Cent.
Ethyl alcohol, sample (i)	0·0050	0·0061 0·0069
,, ,, ,, (ii)	0·0015	0·0022 0·0020 0·0017
,, ,, ,, (iii)	0·0015	0·0020 0·0015 0·0015
Alcohol, to which was added 0·005 per cent. of thiophen and 0·005 per cent. of H_2SO_4. Theory, 0·0048 per cent. of sulphur.	0·0041	0·0045 0·0048

METHOD.—The following is a description of the method:

Apparatus.—This (see Fig. 1) consists of a glass spraying vessel (G) connected by a ground-in joint with a silica tube (H). This in turn is connected with the absorption bottles (K, L and M), in which the combustion products are retained. Details of the construction of the spraying vessel are shown in Fig. 2. The silica tube, which is of translucent silica, is approximately 38 cm. long with a neck 12·5 mm. internal diameter, and walls 1 to 2 mm. thick. A disc of platinum gauze of about 36 S.W.G. is placed in the silica tube about 6·5 mm. above the ends of the spraying tubes. A second disc of platinum gauze is then placed about

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* We are indebted to Messrs. W. G. Bailey and T. Thompson, of Imperial Chemical Industries, Ltd. (Explosives Group), for these determinations.

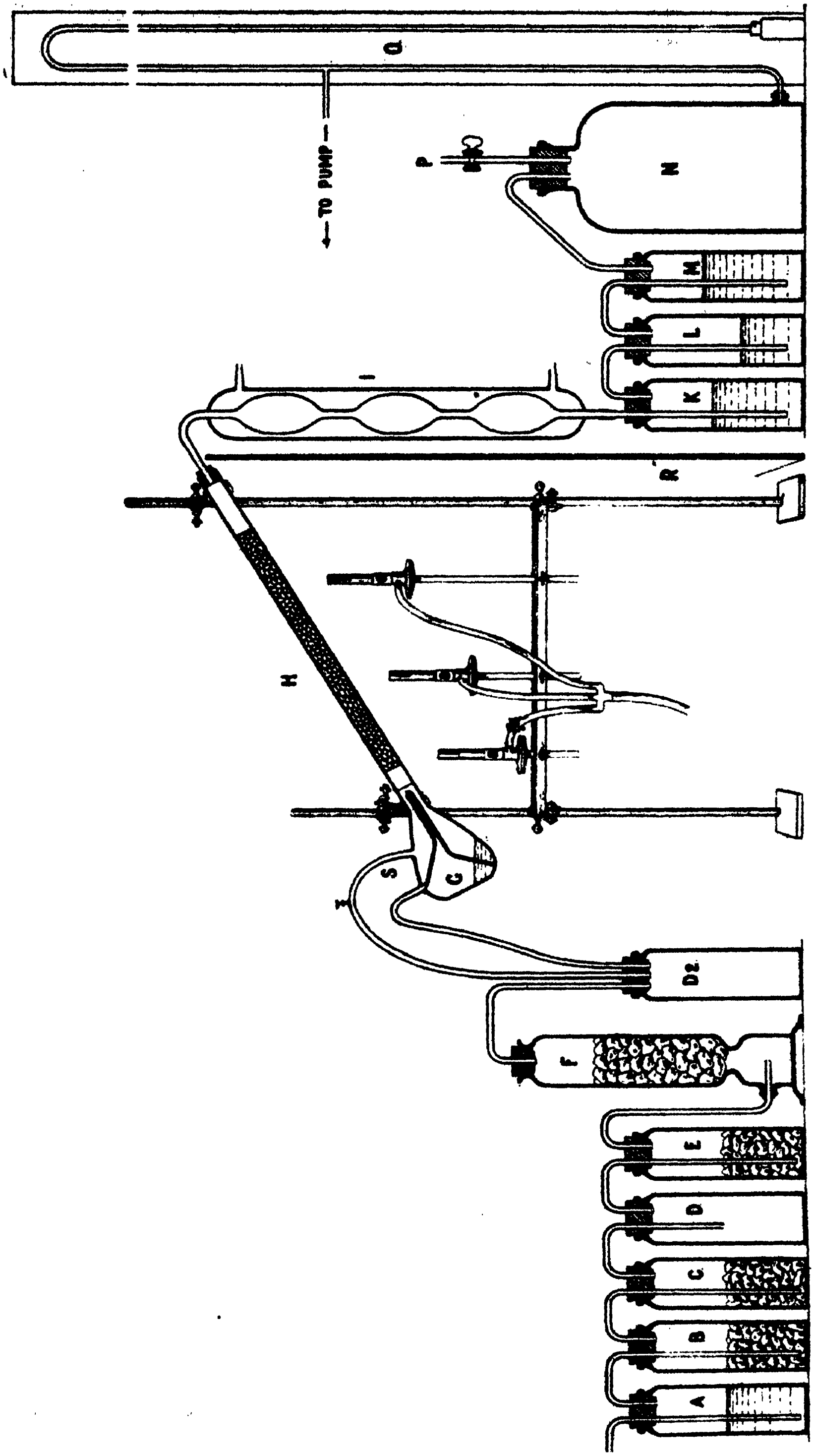

Fig. 1

3·8 cm. above the first, and the tube is filled to about three-quarters of its total length with quartz particles, about 2 mm. in size, platinised by immersing them in 5 per cent. platinum chloride solution, draining off the excess of solution, and igniting them.

A third platinum gauze is placed above the quartz packing, and a short piece of glass tubing, of such length as to come within half an inch of the end of the tube, rests on the last gauze. The last gauze and the glass tube are introduced to prevent the packing from moving in the silica tube.

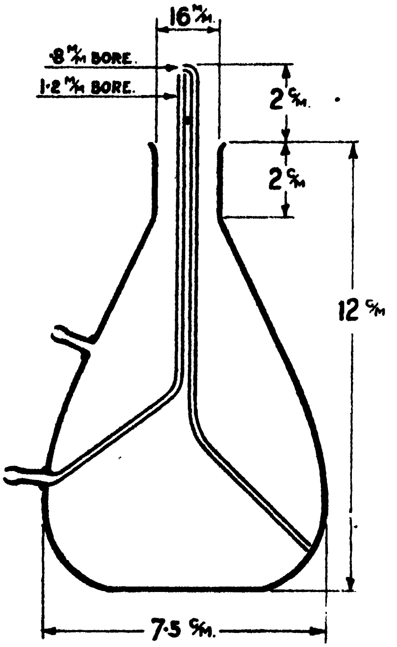

Fig. 2

The quartz tube is inclined at an angle of about 30° to the horizontal, and its upper end is connected, by means of a cork, with a small water-cooled condenser (I), the lower end of which enters the first absorption bottle.

The absorption bottles (K), (L), (M) are each of approximately 200 ml. capacity, and contain freshly prepared 3 per cent. sodium peroxide solution; in (K) 50 ml. and in each of (L) and (M) 25 ml. of the peroxide solution and 25 ml. of water; (M) is connected with an aspirator (N), of about 2 litres capacity, provided with an adjustable air-leak (P); this is employed in regulating the pressure in the apparatus. The aspirator is connected [with a manometer (O) in circuit] with the vacuum pump. A shield of asbestos (R) protects the condenser from the heat of the burners.

The quartz tube is heated by three burners, one placed under the space between the first and second gauzes, the second at a point about 3·8 cm. above the second gauze, and the third at a point about two-thirds of the way along the quartz tube.

The air entering the apparatus is drawn through a purifying train constituted as follows:—(A) containing alcoholic potash (2 *N*) (to absorb carbon disulphide); (B) and (E) containing pumice soaked in 5 per cent. lead acetate solution; (C) and (F) containing pumice soaked in 5 per cent. aqueous potassium hydroxide solution; an empty bottle (D) is placed between (C) and (E) to prevent the solution in (C) being blown over into (E). A trap-bottle (D2) carries the tubes connected with the spraying vessel, the one attached to the auxiliary air inlet (S) being fitted with a screw clip.*

PROCEDURE.—(*a*) *Nitrobenzene and similar bodies.*—A portion of the sample, weighing approximately 15 to 20 g., is placed in the spraying vessel, and the vessel and its contents are weighed. The parts of the apparatus are connected as described, and a gentle stream of air is aspirated through the vessel. The burners are lighted, and the tube is heated to bright redness, except at the point between the first two platinum gauzes at the lower end of the tube; this is maintained at a temperature just sufficient to prevent the collection of liquid above the first gauze. (For benzene and other easily-volatilised liquids the burner under this gauze may be omitted.)

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* The apparatus is obtainable from Messrs. Griffin and Tatlock, Ltd., Kemble Street, Kingsway, London, W.C.2, and at Manchester, Edinburgh, Glasgow and Liverpool.

When the tube is red hot the rate of aspiration is gradually increased until the spraying commences. The rate of air entering through the main and auxiliary inlets is adjusted by means of the tap (P) and the screw clip on (S), so as to maintain a state of bright incandescence at the point above the second burner. The reading of the manometer (O) will vary somewhat with different sets of apparatus, but once the optimum conditions have been established for a particular apparatus, they will serve as a guide in subsequent determinations.

When practically all the sample has been burned the burners are removed and the apparatus is allowed to cool, a gentle current of air being meanwhile drawn through it.

After cooling, the condenser is washed into a 500-ml. beaker, and the contents of the absorption bottles are transferred to the same vessel. The contents of the beaker are boiled to decompose the excess of sodium peroxide, cooled slightly, cautiously acidified with 10 ml. of concentrated hydrochloric acid, and filtered. The filtrate and washings are diluted with water to about 450 ml. and heated to boiling, and the sulphate is separated and weighed as barium sulphate in the usual manner.

The spraying vessel is weighed after the combustion, the weight of the sample used in the determination being found by difference. A well-constructed vessel should retain only about 0·5 g. of the sample.

(*b*) For liquids which do not contain nitro groups, and for solids, the sample is dissolved in about an equal weight of nitrobenzene of known sulphur-content; this solution is then treated exactly as described under (*a*).

Note I.—A small amount of nitrogen acids is formed during the combustion, but it has been found that this is insufficient to interfere with the barium sulphate precipitation.

Note II.—As the glow from the combustion is extremely bright, it is advisable for the operator to wear dark goggles.

The method shows promise of wide application, and work is at present in progress to extend it to the determination of sulphur as a major constituent in some organic compounds.

We wish to record our thanks to Imperial Chemical Industries Limited (Dyestuffs Group), in whose Research Analytical Laboratory this work was carried out, for permission to publish the results of this investigation.

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1. P. Klason, *Ber.*, 1886, **19**, 1910; C. S. Leonard, *J. Amer. Chem. Soc.*, 1923, **45**, 255; E. Wertheim, *ibid.*, 1930, **52**, 1086.
2. British Engineering Standards Association Specification for Motor Benzol, 1921 [135], Appendix III.

BRITISH DYESTUFFS CORPORATION, LTD.
BLACKLEY, MANCHESTER

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

WATER IN BONE MEAL AND IN MEAT AND BONE MEAL

THE proximate analysis of samples of genuine bone flour and of genuine meat and bone meal usually adds up to 98·5 to 99 per cent., but samples of both substances are occasionally met with in which the sum of the moisture, oil, protein and mineral matter amounts only to 90 to 95 per cent. My attention was first drawn to this fact by Mr. John Evans, and the matter has since been investigated here on a number of samples.

Apparently all the meals exhibiting this phenomenon contain a proportion of steamed bone, and the undetermined constituent is undoubtedly chemically combined water that has been introduced during the steaming process. This water is not expelled during the determination of moisture as prescribed by the Fertilisers and Feeding Stuffs Regulations.

The following account of tests made on one sample illustrates the presence of combined water, and the results are typical of those obtained with a number of samples examined:

Steamed bone flour gave the following analytical results:—Moisture, 14·2; oil, 0·2; albuminoids (protein), 3·2; mineral matter, 77·8; total 95·4 per cent.

Five g. of the meal were weighed and subjected to analysis in the following order:

(i) Drying to constant weight at 100° C.:—Moisture, 14·2 per cent.

(ii) Heating for 2½ hours in a closed vessel contained in an oil-bath at 180° C. A current of dry air was drawn over the meal and led into a weighed calcium chloride tube. By this means an additional 3·3 per cent. of water was found.

(iii) Determination of oil on the chemically dry residue. An increase of 0·05 per cent. was found.

(iv) Determination of protein in the oil-free residue. A decrease of 0·2 per cent. was found.

(The determinations of oil and protein in the chemically dried material were made, of course, to prove that the additional water had not been produced by oxidation of the organic matter of the meal.)

The above results clearly indicate the presence, in the sample, of water not detected by the prescribed method for the determination of moisture, and the matter becomes of some importance if a meal contains added carbohydrate in addition to steamed bone. In such a case it is obviously quite inaccurate to estimate the "carbohydrate" by a difference figure between 100 and the sum of the moisture, oil, albuminoids and mineral matter.

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THE DETERMINATION OF ESTERS IN ALCOHOLIC LIQUIDS

VARIOUS organisations, governmental and otherwise, in different parts of the world, which are concerned with the determination of esters in alcoholic liquids, have laid down "official" methods for the purpose. All agree in fundamental principles, and all those whose methods concern me in the course of my duties agree also on one detail, *viz.* that the refluxing of the spirit with excess of hot alkali should continue for an hour. In *Allen's Commercial Organic Analysis* (5th Ed., Vol. I,

p. 257) the suggested time is reduced to thirty minutes. My experience is that even this shorter time greatly exceeds what is analytically necessary.

The following tabulation of some determinations made recently brings out the point excellently:

Sample No.	Volume of $N/10$ sodium hydroxide solution required for hydrolysis of esters Boiled for 10 minutes ml.	Boiled for 30 minutes ml.	Boiled for 60 minutes ml.
1	—	0·25	0·25
2	—	0·30	0·30
3	—	0·60	0·60
4	—	0·80	0·80
5	1·10	1·1	—
6	10·30	—	10·30
7	4·40	—	4·40
8	0·25	—	0·25
9	0·70	—	0·70
10	0·40	—	0·40
11	0·80	—	0·80
12	5·30	—	5·30

The nature of the samples varied from rectified spirit of good quality to illicit spirit. Strengths varied from 26·84 to 61·8 per cent. of alcohol by volume at 60° F./60° F.

In this Laboratory it is often necessary for legal reasons to certify that an analysis has been made by an "official method" of some organisation not under our control. Where a spirit analysis is concerned, this entails a waste of fifty minutes, accompanied by a corresponding "tie-up" of apparatus and bench-space, for every individual sample examined. This is a serious matter for a busy analyst, and it seems very desirable that the organisations concerned in establishing "official methods" should revise some of their preconceived ideas.

This note is published with the approval of Dr. Alfred Tingle, the Chief of this Laboratory.

JAMES HOSSACK

CUSTOMS-EXCISE LABORATORY
DEPARTMENT OF NATIONAL REVENUE
OTTAWA, CANADA

COLOUR REACTIONS OF CARBAZIDES AND CARBAMIDES WITH DIACETYL AND DIACETYLDIOXIME

ON warming semicarbazide hydrochloride and diacetyldioxime with hydrochloric acid it was found that an intense permanganate-red colour developed, reaching a maximum intensity after a few minutes. The colour was permanent and apparently stable for several days. A similar colour was produced by using diacetyl in aqueous solution instead of diacetyldioxime, but the time of development was not appreciably shortened. On the subsequent addition of ammonia bluish-violet colours appeared.

The intensity of the red colour varies with the relative proportions of diacetyl or the dioxime and semicarbazide, and with the acidity of the solution; increasing the acidity favours the formation of a more intense colour.

The following results were obtained in an attempt to discover to what extent these effects were characteristic of semicarbazide:—Hydrazine, guanidine, nitroguanidine, aminoguanidine, dicyandiamide, oxamethane, semi-oxamazide, oxalic dihydrazide, sym. diphenylthiocarbamide, phenylthiosemicarbazide and asym. dibenzylhydrazine gave very pale yellow or practically colourless solutions when gently heated with either diacetyldioxime or diacetyl in the presence of hydrochloric acid.

Carbamides, semicarbazides and certain other compounds gave definite colours, as shown in the following table:

Substance	Diacetyldioxime and hydrochloric acid	Diacetyl and hydrochloric acid
Semicarbazide	Red	Red
4-Methyl- ,,	Red	Red
4-Phenyl- ,,	Red	Red
4-*m*-Tolyl- ,,	Red	Very pale pink
4-*p*-Tolyl- ,,	Reddish-brown	Red
4-*p*-Bromphenyl- ,,	Reddish-brown	Red
4-Benzyl- ,,	Red	Reddish-yellow
4-β-Naphthyl- ,,	Brown	Brown
4-as.*m*-Xylyl- ,,	Red	Red
1-Phenyl- ,,	Reddish-brown	Red
1-β-Naphthyl- ,,	Brown	Brown
Carbamide	Brown	Bright yellow
Methylcarbamide	Reddish-brown	Pale pink turning to bright yellow
o-Tolylcarbamide	Brown	Red
m-Tolylcarbamide	Brown	Red
Benzylcarbamide	Brown	Reddish-brown
Diphenylcarbazide	Red	Red
Phenylhydrazine	Brown	Yellow
Phenol	Pink	Yellow
Aniline	Pale violet	Very pale pink
m-Toluidine	Pale violet	Very pale pink

1-Phenylsemicarbazide gives a red colour with hydrochloric acid alone, but this does not survive a few minutes' heating in a boiling-water bath; if diacetyl is present, a permanent deep red colour is produced.

The addition of a slight excess of ammonia after the development of a colour in acid solution yielded a pale yellow or colourless solution in all cases except with semicarbazide and 4-methylsemicarbazide (blue or violet), 1-phenylsemicarbazide (reddish-brown), and carbamide (bright yellow).

The results shown above should be useful for rapid qualitative tests; thus, semicarbazide is readily differentiated from hydrazine, semi-oxamazide, aminoguanidine and oxalic dihydrazide by the formation of a red colour, and also from all the other compounds mentioned, with the exception of 4-methylsemicarbazide, if the solution is finally made ammoniacal. The sensitivity with semicarbazide is such that about 0·1 mg. may be detected in a few ml. of a solution made strongly acid with hydrochloric acid.

I wish to thank the Air Ministry for granting facilities for carrying out this work.

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BUTYRISED FATS: BUTTER-AROMA

When a full-flavoured butter is distilled with steam, free butyric acid can be identified in the distillate, which also contains a neutral compound yielding butyric acid on saponification. The use of butyric cultures, ethyl butyrate or butyric acid in margarine has been tried experimentally, but with unsatisfactory results. Butyric acid itself is too fugitive, and search was therefore made for a parent substance which would continuously yield traces of the free acid. In experiments with margarine which had been prepared with skim-milk properly soured with lactic streptococci, including aroma bacteria, it was found that a small addition of tributyrin caused the mass to be gradually pervaded by a pleasant butter-aroma. Unfortunately, the flavour was spoilt by the bitterness of the tributyrin; this was obtained from various sources, and was synthesised, fractionated and refined, but in no instance was the bitterness avoided. Glycol dibutyrin produced a similar aroma in margarine, but had also an inherent nasty flavour. Mixed butyric triglycerides were then prepared, and the flavour of these indicated that the butyric acid in butter-fat must be present as a mono-butyric triglyceride, with butyric acid in the β-position. The bitterness of tributyrin is due to the butyric acid in the α-position.

Coconut oil was butyrised by heating it with butyric acid at 160° C. After 2 hours' treatment the neutralised fat gave Gilmour butyric numbers equivalent to 3 per cent. of butter, and to 116 per cent. after 36 hours' treatment. Fat can also be butyrised by heating it with tributyrin in presence of a suitable catalyst, such as 1 per cent. of stannous hydroxide, at 200° to 250° C., the mixture being agitated by causing an inert gas to bubble through it. Coconut fat containing from 5 to 15 per cent. of tributyrin was free from bitterness after 2½ to 7 hours, whilst arachis oil with 25 per cent. of tributyrin required 11 hours' treatment.

The results of several investigations of aroma-producing substances of the acetoin (acetyl-methylcarbinol), 2·3-butylene glycol, and diacetyl-type have recently been published. The quantity of diacetyl (the substance to which the aroma of butter is mainly due) in butter ranges from 0 to 5 parts per million, this depending on the presence (and proportion) of aroma bacteria in the souring cream. My experiments (in which I was assisted by Mr. Kenneth Wallis) have definitely indicated, however, that the composition of the fat is an important factor in the production of aroma.

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Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

SOLUTION OF IODINE: USE OF METHYLATED SPIRIT

AT Salford City Police Court on the 4th January summonses were heard in connection with the sale of a bottle of solution of iodine. The sample was certified by the Public Analyst to contain 0·7 per cent. of iodine, 0·7 per cent. of potassium iodide, 72·2 per cent. of methylated spirit (90 v/v), 2·5 per cent. of boric acid, and 23·9 per cent. of water, and, upon comparison with the British Pharmacopoeia formula for Liq. Iodi. Mitis, to be 71 per cent. deficient in iodine, and 53 per cent. deficient in potassium iodide, to contain the foreign ingredient, boric acid, and to have the alcohol of the Pharmacopoeia replaced by a smaller amount of methylated spirit. The retailer was summoned under Section 2 of the Food and Drugs (Adulteration) Act, and the makers under Section 5 of the Summary Jurisdiction Act, 1848, for aiding, abetting, counselling and procuring the sale. The makers were also summoned under Section 30 of the Food and Drugs (Adulteration) Act for wilfully applying a false label. Both retailer and maker pleaded guilty.

A feature of the case was the statement by the makers that their formula had been approved by the Commissioners of Customs and Excise. One of the objects of the prosecution was to make it clear that when the formula of a preparation containing industrial methylated spirits is approved by the Commissioners of Customs and Excise, such approval merely signifies that they are satisfied that the spirits will be used in accordance with the provisions of the Spirits Act, 1880, and amending Acts, and does not imply that the resulting article will comply with the Food and Drugs Act or with any similar Act.

Mr. P. Butlin, appearing for the prosecution, said that this case was intended to serve as a warning. The Stipendiary Magistrate, Mr. Percy Macbeth, therefore imposed nominal penalties of five shillings in each charge, but ordered the makers to pay seven guineas costs.

The same penalties were inflicted in two similar cases concerning other brands of iodine solution.

"REAL CREAM" TARTS

At the West London Police Court, on August 9th, 1934, a confectioner was summoned by the Hammersmith Borough Council for selling "Real Cream Tarts" and "Real Cream Cookies" which were not of the nature, substance and quality demanded. Evidence was given that samples were purchased at the defendant's premises from a quantity of cakes and pastries displayed in the window and bearing tickets with the words "Real Cream, 4 for 3½d." The certificates of the Public Analyst (Mr. F. W. Edwards, F.I.C.) showed that the samples contained a filling resembling cream, made from a fat having the characteristics of margarine fat, and therefore consisted of a substance other than real cream.

The defendant, who pleaded guilty, was fined £2 10s.

At the same Court a firm of bakers was summoned for a similar offence in respect of the sale of a "Real Cream Sandwich." The defendants, who pleaded guilty, stated that a wrong ticket had been used by an assistant.

The summons was dismissed on payment of £2 2s. costs.

A summons was also brought against another Hammersmith confectioner in respect of the sale of "Real Cream Éclairs." In this case the pastries were displayed in the shop window bearing a ticket "Real Cream Éclairs—2d. each." The Public Analyst certified that the filling contained 51·7 per cent. of fat other than milk-fat, and therefore consisted of a substance other than real cream.

The defendant, who pleaded not guilty, was fined £5.

Department of Scientific and Industrial Research

REPORT FOR THE YEAR 1933–4*

IN the introduction to the Report of the Committee of the Privy Council for Scientific and Industrial Research (pp. 1–5) it is mentioned that the most important of the proceedings during the year concerned the provision of further grants to Research Associations to be offered on conditions that would secure a larger measure of support from the industries benefited. The Building Research Board has been reconstituted to conform with the general principles adopted for Research Boards, and a Standing Conference on Timber Utilisation has been established.

During the year fifteen British patent applications have been filed, and ten British patents have been allowed to lapse; the subject-matter of these patents is given.

The Report of the Advisory Council to the Committee of the Privy Council (pp. 7–22) discusses the question of grants to the various Research Associations, and lays emphasis on the immediate practical advantages that industry can derive from adequate support and use of research associations. Certain researches have been transferred from Government control to the supervision of industry, and co-operation in research with the Dominions overseas has been continued, notably in connection with the storage and transport of food.

The researches for Government include the investigations of the conditions of safety for the transport of gas cylinders, and for the production of cheap and efficient respirators to be used against the inhalation of dust. Another important development has been the establishment of a large-scale fire-testing station in London by the Fire Offices Committee of the insurance offices in consultation with the Building Research Station. The third section of the Report (pp. 25–95) gives a summary of the research work done during the year.

NATIONAL PHYSICAL LABORATORY.—Work has been continued on the fundamental standards of length, mass, electrical resistance and current, candle-power, temperature, and X-ray intensity.

It has been found that up to about 900° C. iron has a negative temperature coefficient of thermal conductivity, but that gamma iron appears to possess a positive temperature coefficient.

A further advance in the standardisation of X-ray measurement has been made by the completion of the investigation of calibration by measurement of the colour-change of barium platinocyanide pastilles when exposed to X-rays. In the Photometry Division photo-electric methods of photometry have been developed, *e.g.* for the detection of non-uniformity in the candle-power of a lamp.

Metrology Department.—The researches having for their ultimate object the establishment of a wave-length standard of length have reached a further stage in the determination of the lengths of the yard and the metre in terms of the red radiation of cadmium, both in air and *in vacuo.*

Metallurgy Department.—Progress in the study of the physical structure of metals and alloys has been made. The production of iron of high purity has received further attention; in recent samples the total impurities, excluding oxygen, amount to only 0·012 per cent., the nickel present having been reduced to 0·0006 per cent. The study of the properties of molten metals and alloys has also been continued.

FUEL RESEARCH.—The Report of the Fuel Research Board for the year ended March 31st, 1934, has recently been published (see ANALYST, 1934, **59**, 540).

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* H.M. Stationery Office, pp. 183. Cmd. 4787. 1935. Price 3s. net.

FOOD INVESTIGATION.—For the Report of the Food Investigation Board for the year 1933 see ANALYST, 1934, **59**, 696.

BUILDING RESEARCH.—Details of the work carried out at the Building Research Station during the year are given in the Annual Report of the Building Research Board (*cf.* ANALYST, 1934, **59**, 755). The general research is now steadily advancing to the stage at which there is a definite scientific basis for the utilisation of building materials and methods of construction.

STEEL STRUCTURES RESEARCH.—The Committee has issued a second report, in which the investigations are dealt with under four headings: the measurement of strains in existing buildings; the examination of bolted and riveted connections; stress analysis, and the study of new methods of design.

ROAD RESEARCH.—The comprehensive scheme of road research visualised by the Road Research Board has been described in the first Annual Report of the Board. The subjects dealt with include road construction, processes, road usage, and the development of special testing plant.

FOREST PRODUCTS RESEARCH.—The sixth report of the Forest Products Research Board deals *inter alia* with the factors determining the technical qualities of timber, the investigation of the insects and fungi that destroy wood, and the application of analytical methods to anatomical measurements of various timbers and to the study of the variations that occur in the wood-cells.

WATER IN WOOD.—It has been found that practically all the water in wood up to the fibre saturation point is held by adsorption, and that the method employed in the investigation has immediate applications of a practical nature in affording a means of measuring directly the fibre saturation point of various woods. Experiments have demonstrated that the common belief that timber becomes less affected by changes of moisture-content as it ages has no foundation in fact, and that there is no material difference between old and new timbers in the amount of shrinkage or expansion that takes place with a given variation in moisture-content.

METALLURGICAL RESEARCH.—The work is surveyed under the following headings: Behaviour of Materials at High Temperatures, Research on Light Alloys, Steel Castings, Alloy Steels, Gases in Metals, Cracking of Boiler Plates, Oxides in Steel, Oxidising Power of Basic Slags, Rust Prevention (see Engineering Research Special Report No. 12, H.M. Stationery Office, 1934; price 6d. net).

WATER POLLUTION RESEARCH.—The progress in the Department's work in relation to water supplies and the prevention of pollution is summarised in the Annual Report of the Research Board (ANALYST, 1935, 37).

CHEMICAL RESEARCH.—Among the activities of the Laboratory to which special reference is made are corrosion research, chemical reactions under high pressure, tar research, chemotherapy, water pollution, microbiology, dental investigation, and chemical engineering.

COLOURING MATTER IN HEAVY OILS.—A long investigation into the nature of the colouring matter of heavy oils of low-temperature tar has shown that these coloured substances are hydrocarbons of the naphthacene class.

The mixture of higher tar acids used as a wetting agent under the name of "Shirlacrol" has been obtained in considerable quantities from low-temperature tars and vertical-retort tars.

CHEMOTHERAPY.—The outstanding feature of research in chemotherapy has been the preparation of a potent arsenical drug, succinanilidomethylamide-*p*-arsonic acid; this is being tested clinically.

Synthetic Resins.—In connection with the study of synthetic resins it has been found that polyhydric phenols condense readily with formaldehyde to form resins with remarkable adsorptive power for metallic cations—a property of significance in water purification.

Sensitive Test for Ferrous Iron.—In comparative experiments on the dehydrogenation of pyridine in the presence of different anhydrous metallic chlorides two products, 2:2′-dipyridyl and 2:2′:2″-tripyridyl, were found to afford a delicate test for ferrous iron. Samples of these have been distributed to various enquirers.

ILLUMINATION RESEARCH.—Work on the glaring effect of coloured light sources and the "time effect" of glare is continuing, and a glare-meter has been designed. Problems of mine lighting have been discussed, and the investigations in progress for the British Standards Institution on the fundamental properties of glassware have now been completed. The colorimetric examination of artificial daylight units on behalf of the B.S.I. has also been completed, and a report has been communicated to that Institution.

LUBRICATION RESEARCH.—The problems investigated include journal friction, oscillating bearing experiments, and experiments on the oxidation of oils.

ATMOSPHERIC POLLUTION.—The Report of the Atmospheric Pollution Research Committee (ANALYST, 1934, **59**, 280) includes a new method for obtaining an indication of sulphur pollution in the air.

FABRICS RESEARCH.—A report, including the large-scale tests of methods for fire-proofing fabrics, is to be published.

INDUSTRIAL RESPIRATORS.—A new design of respirator, which will not interfere with the vision of the wearer, is being developed.

RESEARCH ASSOCIATIONS.—As in previous years a brief account is given of the work of Research Associations during the year (pp. 97–134). Among these the Reports of the British Association of Research in the Chocolate, Sugar, Confectionery and Jam Trades and of the British Food Manufacturers' Association contain numerous points of special analytical interest.

Gelatin.—The effects of variations in the physical properties of commercia gelatins have been studied, with special reference to the manufacture of marsh mallows.

Pectin.—Pectin may vary in composition with the kind of fruit from which it is extracted and the method of extraction used. The formation of bubbles in jelly and premature setting of jelly, which are a frequent source of trouble to the jam manufacturer, are caused by the extracts of certain fruits. Purified pectins are therefore being prepared from these fruits, and their chemical and physical properties are being studied with a view to finding an explanation and a remedy.

Starch.—Starch, like pectin, is a complex substance, and its properties vary according to its source and method of preparation. An investigation of the properties other than its jellifying power is in progress.

Determination of Salt in Cured Meats.—An apparatus has been adapted to the purpose of determining the proportion of salt in bacon, etc. In the modified form it will be possible to read the percentages of salt direct from an indicator, the test taking only a few minutes. By means of this instrument it has already been found possible to determine the thickness of the fatty layers in bacon or pork, and thus to grade carcases in this respect.

Salt Tolerance of Bacteria.—Work on this subject has been continued, and information on variations in the percentages of salt required to inhibit the growth of various bacteria has been accumulated. Fortunately, some of the most objectionable forms appear to be the most easily suppressed.

Ministry of Agriculture and Fisheries

RETAIL TRADE NAMES FOR FISH

THE following letter has been sent by the Ministry to the Clerks of Local Authorities administering the Food and Drugs (Adulteration) Act:

RETAIL TRADE NAMES FOR FISH. *Re* FISHERIES NOTICE NO. 23

SIR,

I am directed to state that the Ministry of Agriculture and Fisheries has had under consideration the possibility of effecting some measure of standardisation of the names under which different kinds of sea fish are sold to the public.

Your Authority are probably aware that there have recently been a number of prosecutions of fishmongers by certain Local Authorities under the terms of the Merchandise Marks Acts and the Food and Drugs (Adulteration) Act, 1928, for selling fish under false trade descriptions. As a result the National Federation of Fishmongers approached the Ministry and suggested that a standard list of retail names of all the principal varieties of fish should be drawn up for the information of fishmongers who were in many cases in doubt at the present time as to what names might properly be used. It was explained to the Federation that neither the Ministry nor any other body had power to prescribe or legalise the use of particular names; the legality of any name in the event of dispute could only be determined by the Courts. Nevertheless, the Ministry thought that certain advantages would accrue if an agreement could be reached among the principal Associations of fish merchants and traders on the use of a standard list of names which would be recommended by the Associations to their members.

With this object in view a list has been drawn up after consultation with the principal Associations concerned. So far as possible the ordinary recognised names for the various kinds of fish have been adopted. In a few instances, however, where these names were liable to be confused with those of other kinds of fish or were so unpleasing in themselves as to be likely to prejudice the sale of the fish to the public (*e.g.* cat-fish or dog-fish) a different name has been suggested, care being taken in no case to propose a name which might be confused by the public with that of some other known variety of fish.

In a few cases where different names are known to be in common use in particular localities for the same kind of fish, alternatives have been shown. In order to simplify the list and to secure as much uniformity as possible, alternative names have been introduced very sparingly, but it is of course possible that other established local names may be in use which are not misleading to the public and to which therefore no objection could reasonably be raised on that ground.

As previously indicated, this list is being recommended by the various Associations to their members for general adoption. The Ministry thinks, therefore, that the list will be of use to those Local Authorities by whom action under the Merchandise Marks Acts or the Food and Drugs (Adulteration) Act is likely to be taken in the event of fish being sold under false trade descriptions. Further copies of the list may be obtained from the Ministry on request.

I am, Sir, your obedient servant,

(*Signed*) H. G. MAURICE

To the Clerk of the
Council or Town Clerk

FISHERIES NOTICE No. 23

The list contains in six pages the suggested trade names, the scientific names, and the general English equivalents of 53 species of fish, with synonyms in brackets. The suggested new trade names include the following:

Argentine (*Argentina sphyraena* and *A. silus*) for Lesser silver smelt, Great silver smelt.

Atherine (*Atherina presbyter* and *A. boyeri*) for Silver sides, Smelt, Sand smelt, Atherine, Sea smelt.

Forkbeard (*Urophycis blenoides, Phycis blenoides, Raniceps raninus*) for Greater forkbeard, Forked hake, Lesser forkbeard.

Lance (*Ammodytes lanceolatus, A. tobianus, A. cicerulus*) for Greater sand eel, Small sand eel, Smooth sand eel, Lance.

Redfish (*Sebastes marinus, S. norvegicus, S. viviparus, S. heltzeni, Scorpaena dactylopera*) for Norway haddock, Soldier.

Roughback (*Hippoglossus platessoides, H. linianoides, Drepanopsetta platessoides*) for Long rough dab.

(See also Hattersley, ANALYST, 1935, 69.)

Cyprus

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1933

THE Government Analyst (Dr. S. G. Willimott) states that, of the 2342 samples examined, 2321 were submitted officially, 1073 being samples of food and drugs, and 229 exhibits in connection with criminal cases. For the purpose of the administration of the Food and Drugs Law the Island is divided into seven districts. Samples are taken by the District Sanitary Inspectors, and the control over the food supply is increased by authorising certain sanitary inspectors, who hold the Local Sanitary Certificate, to take official samples in their sub-districts.

MILK.—Fifty-four of the 172 samples examined were adulterated, and there is ample evidence that the adulteration of fresh milk is widespread throughout the Island. A more stringent requirement for fat-content than the present 3 per cent. might prove effective (*cf.* Annual Report for 1932; ANALYST, 1934, **59**, 41).

OLIVE OIL.—Forty of the 68 samples of olive oil examined were adulterated, and it was difficult to obtain a genuine article in the town of Nicosia. Owing to the drought the harvest of olives was poor, and the fact that the supply of olive oil was restricted was regarded as an opportunity and justification for wholesale adulteration. In some cases material sold as olive oil was found to consist entirely of soya-bean oil.

CANNED FISH.—The District Sanitary Inspectors, acting on instructions, again devoted particular attention to the stocks of canned foods, and it was found necessary to condemn some thousands of cans of unfit material. Merchants are now showing more caution by ordering smaller stocks, and thus avoiding the exposure of large consignments to long-continued heat. It has been found, for example, that canned fish in tomato sauce is very liable to be spoiled by exposure to the Cyprus summer, and shopkeepers have been advised accordingly. As a result of the last four years' work there is now a definite improvement throughout the Colony in the condition of canned food.

COFFEE.—Starch continues to be the favourite adulterant, 37 of the 187 samples examined containing from 5 to 60 per cent.

NITROBENZENE POISONING.—An unusual case of non-fatal poisoning at Amiandos was investigated. A tin of water-proofing composition, containing nitrobenzene as solvent, had been left for some time in a closed office during the summer, and vapour had escaped and produced symptoms of faintness and nausea in a young clerk. It is known that nitrobenzene vapour is toxic (*Taylor's Medical Jurisprudence*, 1928, Vol. II, p. 699), and this appears to be the explanation of the effects in this case.

CAUSTIC SODA POISONING.—It is somewhat remarkable that in one year there should have been 8 cases of poisoning by caustic soda in Cyprus, an island with a population of only 348,000. Four of these cases were the results of accidents to young children, and the remainder were cases of suicide. In every instance the alkali was derived from supplies used for domestic washing purposes, to soften the generally prevailing hard waters of Cyprus, but, as the result of recent experience, it was advised that caustic soda and caustic potash should be placed on the Poisons Schedule. This recommendation was adopted by Government in February, 1934. Formerly the alkali used as a water softener consisted exclusively of wood ashes, but within recent years this has been replaced by washing soda, and during the last two years by caustic soda.

The first case of poisoning occurred in December, 1932, and an account of it was published in *The Lancet*, August 19th, 1933. The caustic soda, as sold, consisted of fused lumps, and analysis showed an average of 77 per cent. of sodium hydroxide with 10 per cent. of sodium carbonate. Four cases of this series, all affecting adults, have been studied in some detail. The fatal dose of caustic soda is unknown, but Starkenstein (*Toxikologie*, Berlin, 1929, p. 91) considers it to be from 10 to 20 grams of the solid material. From our experience it must be much less than this, because even five grams has produced the most serious complications of stricture, culminating fatally in 74 days. There was perforation of the oesophagus in one fatal case, and possibly perforation of the stomach in another; in another three cases stricture had developed. The pathology of certain of these cases has been studied by the Bacteriologist, and a joint paper embodying these results was published in the *British Medical Journal* (June 9, 1934, p. 1022).

CYPRUS WATER SUPPLY.—Owing to the continuance of the drought, the water problem remained urgent throughout the year, and many old sources went dry during the summer. There was intensive search for water, and a number of schemes were launched, some of which were successful. Altogether 67 samples, mostly new supplies, were analysed, of which 14 were returned as unsatisfactory for drinking purposes. It is encouraging to observe a more extensive use of iron pipes, in contrast with the old system of ground aqueducts, for the conveyance from the source to the point of distribution of public and private water supplies. Water conveyed by aqueduct is nearly always open to contamination, especially in Cyprus, where chlorination is not practised, while the loss by leakage and theft must be considerable. A marked improvement in the quality of the water supply, both in town and village, can be expected when the system of piping supplies has become general.

The character and quality of water supplies in Cyprus vary widely from the pure soft water of the mountain spring to the hard, saline and often polluted waters of the plains. The constituents of the water also frequently vary widely with the different seasons of the year.

British Guiana

REPORT OF THE GOVERNMENT ANALYST, 1933

THE Government Analyst (Mr. K. Wallis) reports that the total number of samples analysed during the six months ended June 30th, 1933, was 2485, of which 106 were adulterated. As usual, the bulk of the samples consisted of milk, 98 of the 2204 samples being adulterated. The average percentage of fat in the genuine samples was 4·0, showing that the minimum of 3·25 per cent., fixed by the Sale of Food and Drugs Ordinance, is ample for average milk from the cows in the Colony.

Surprise raids at frequent intervals, on Sundays, Public Holidays and at times outside official hours, are necessary. Forty-three of the 568 samples of milk thus taken on 25 occasions were adulterated. All milk is strained by the vendors, so that none of the 52 samples tested contained dirt.

Of the other 281 samples of food examined, 8 did not comply with the requirements of the Ordinance, three samples of butter consisting wholly of margarine. Two samples of aerated drinks contained saccharin, the use of which in such products is prohibited.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection of Trichlorotribenzylidenesorbitol by means of Acetone. G. Reif. (*Z. Unters. Lebensm.*, 1934, **68**, 468–473.)—The method of detecting benzylidenesorbitol by means of acetone and sulphuric acid (ANALYST, 1934, **59**, 44) for ascertaining the presence of fruit-wine in wine may be adapted to apply to Litterscheid's method of detecting sorbitol (ANALYST, 1932, **57**, 178). When treated with sulphuric acid, the trichlorotribenzylidenesorbitol formed in this method gives *o*-chlorobenzaldehyde, and this, with acetone, gives *o*:*o*-dichlorodibenzylideneacetone, which dissolves in the sulphuric acid to form an orange-red solution. Trichlorotribenzylidenesorbitol is, however, more difficult to resolve into its components than the corresponding chlorine-free compound, so that stronger sulphuric acid is required. Prior to its decomposition with acid the chlorobenzylidene compound must be purified by thorough washing with methyl alcohol. Details of the procedure are given. T. H. P.

Determination of Rancidity in Flours, Semolinas and Italian Pastes. J. Berlie. (*Ann. Falsif.*, 1934, **27**, 552–553.)—Further experience of the method for determining rancidity (ANALYST, 1934, **59**, 629) has led to certain modifications being adopted. With substances poor in fat, such as flour, 5 g. of material should be taken, and where a high percentage is present, as in wheat germ, powdered egg, etc., 0·5 to 1 g. The extraction method should follow the French official method for flours, but 40 ml. of a mixture of 40 parts chloroform, 30 parts ether, and 30 of 95 per cent. alcohol, should be used, and to the collected extract 5 ml.

of an alcoholic solution of potassium iodide are added (5 g. in 200 ml. of alcohol and 50 ml. of water). After standing for 24 hours in the dark, the mixture is titrated with 0·002 *N* sodium thiosulphate solution. The degree of rancidity for 1 g. of fatty substance is the number of ml. of thiosulphate required for 100 g. of the product, divided by the percentage of fatty substance present, and the index of rancidity is the above-mentioned figure multiplied by 0·000254. From a number of experiments rancidity appears to manifest itself when the index for 1 g. of fatty substance is 0·01 or more. D. G. H.

Preliminary Tests for the Detection of Small Amounts of Hydrogenated Oils, Tallow and Fats of the Palm-fat Group in Lard. A. Peter. (*Z. Unters. Lebensm.*, 1934, **68**, 521–530.)—For the detection of hydrogenated oil or tallow, use is made of the fact that the glycerides crystallising from lard under certain conditions have a lower specific gravity than the crystals of α-palmitodistearin of tallow or the tristearin of hardened oils. The lard is filtered through a dry filter-paper and 5 g. are weighed into a thick-walled bacteriological test-tube, 170 mm. long and of 15 mm. bore, which is then left for 20 to 24 hours at 10 to 18° C. In order to ensure uniformity of conditions, not more than 12 samples should be tested in one batch. A stand holding the samples is left in an oven at 105° C. for 30 to 40 minutes, after which the stand is removed from the oven and the tubes immersed singly in a water-bath at 45° to 46° C. Exactly 5 minutes after the removal of the stand from the oven the first tube is taken from the bath and quickly wiped. Exactly 5 ml. of ether at 22° to 23° C. are run in rapidly from a burette, the tube being then closed with a rubber stopper, shaken five or six times, and placed in a bath at 20·5° C. The other tubes are similarly treated in order. Twenty minutes after removal from the bath at 45° to 46° C. the first tube is taken from the 20·5° C. bath and wiped, 6 ml. of alcohol (sp.gr. 0·80783 at 15° C.) at 22° to 23° C., being run in from a burette, and the tube closed and shaken as before, and placed vertically in a stand. All the tubes are left for 2½ hours in an incubator at 23·5° to 24° C., and afterwards shaken by four or five brisk movements and returned to the stand. Any tube in which the upper phase undergoes rapid de-mixing with sudden clearing, while the lower phase forms a turbid emulsion, is held by the stopper and inverted two or three times. After the lapse of 10 to 15 minutes, the tubes are examined. Samples forming no deposit contain at most small proportions of tallow or hardened oil, but if any appreciable thick deposit forms, the sample should be tested for tallow or hardened oil by Bömer's method (ANALYST, 1914, 39, 84). When hardened oil is present in only small amount, the lower phase often demixes rapidly, whilst the upper phase forms an emulsion including the solid glycerides. In this case, hardened oil is indicated by the powdery, crystalline deposit forming in the lower phase and keeping the liquid above the deposit turbid for some time. To ensure that the alcohol used is of correct strength, 1·5 litre of 96 per cent. alcohol is distilled with 300 g. of lime from a 2-litre fractionating flask until the whole of the alcohol has passed over. To the distillate 96 per cent. alcohol is added until 6 ml. of the product, 5 ml. of ether and 5 g. of fat melted from bacon and cooled to about room temperature shows the mixing temperature 31·5° to 32° C. (see below).

As a preliminary test for coconut oil or palm-kernel oil in lard, use is made of the mixing temperature. Two grams of the anhydrous lard are placed in a bacteriological test-tube (170 × 15 mm.), 6 ml. of glacial acetic acid of definite water-content are run in from a burette, and then exactly 1 ml. of xylene from a micro-burette. The tube is at once closed with a rubber stopper carrying a small-bulbed thermometer reading to 0·1° C., the bulb being at the middle of the column of liquid. If the fat sets after being weighed out, it is re-melted and cooled to about room temperature before the acetic acid and xylene are added. The tube is then heated and carefully shaken over a flame until a homogeneous liquid phase forms; it is then fixed, by means of a cork, inside a wider tube. The liquid is next shaken until it becomes permanently turbid, the mixing temperature being read off to within 0·1° C. Results are given for a number of lards of various origins, after addition of 5 or 20 per cent. of coconut oil or palm-kernel oil. For Yorkshire lard, with the refractometer reading (Zeiss butyro-refractometer) 49·0 at 40° C. and the mixing temperature 46·6° C., this temperature becomes 43·6° (43·0°) or 35·3° (34·8°) on addition of 5 or 20 per cent. of palm-kernel oil (coconut oil). To ascertain the suitability of the acetic acid, use is made of fat rendered from bacon and having the acid value 0·6 to 1·2, and the butyro-refractometer value 50 to 50·4 at 40° C. The acetic acid should contain so much water that the mixing temperature of 2 g. of this fat, 1 ml. of xylene and 6 ml. of the acetic acid is 43·5° C. If the temperature found differs from this by less than 1°, the acetic acid may be used and the results obtained corrected accordingly. The theoretical aspects of the above tests are discussed at length. T. H. P.

Deterioration Value [Verdorbenheitszahl]. Iodimetric Determination of the Oxidised Products in Fats and Oils. J. Gangl and W. Rumpel. (*Z. Unters. Lebensm.*, 1934, **68**, 533–539.)—The deterioration of edible fats and oils which finally renders them unfit for food is due essentially to oxidation processes, and in its early stages consists of combination of oxygen at particularly reactive double linkings. If dried in the air with a large surface exposed, beef-fat and lard may take up quantities of oxygen representing an increase in weight of 3 per cent. The extent to which this change has proceeded may be determined iodimetrically (*cf.* Taffel and Revis, *J. Soc. Chem. Ind.*, 1931, **50**, 87T; abst. ANALYST, 1931, **56**, 323), and is termed the "deterioration value," this being defined as the number of milligrams of potassium iodide decomposable by 10 g. of the fat.

For the determination the following solutions are required: (i) 0·01 *N* potassium iodate solution. (ii) A solution of 4·4 g. of potassium iodide in propyl alcohol (free from impurities reacting with iodine). The titre is ascertained by diluting 5 ml. with 20 ml. of hydrochloric acid (1 : 1), adding 10 ml. of 10 per cent. potassium cyanide solution and 3 ml. of starch solution, and titrating and shaking with the iodate solution (i) to decolorisation. (iii) Ten per cent. potassium cyanide solution. (iv) Two g. of soluble starch and 0·01 g. of mercuric iodide (as preservative) are ground with a little water and poured into 1 l. of boiling water. The clear solution undergoes no change even on long storage in a colourless glass vessel, but, if for any reason, it gives a violet instead of a pure blue colour with dilute iodine solution it should be discarded.

Ten grams (5 if the fat has undergone much change) of the fat are treated, in a 200-ml. flask with a ground stopper, with 5 ml. of solution (ii) and 2 drops of glacial acetic acid. The flask is kept for about 10 minutes (5 minutes suffice with a much-altered fat) in a bath at about 50° C., with occasional vigorous shaking. After being well shaken with 20 ml. of hydrochloric acid (1 : 1) and left for a short time, the liquid is poured through a moistened filter and the flask and filter are washed with repeated small amounts of the hydrochloric acid (1 : 1), care being taken to wash the fat thoroughly. The filtrate, which may be slightly turbid, is treated with 10 ml. of solution (iii) and about 3 ml. of (iv), and is titrated with solution (i), the end-point being sharp: 1 ml. of 0·01 *N* iodate ≡ 1·66 mg. of potassium iodide.

With practice the titration may be carried out, although not so easily, in presence of the fat. The end-point is then reached when a drop of the iodate solution just decolorises the aqueous layer, subsequent appearance of a blue colour being neglected. Fresh edible fats give deterioration values of about 3 to 5, whilst, for fats which have become rancid and nauseous, values up to 20 may be obtained. In judging the condition of fats, these values are considered in conjunction with the acidities and the Kreis values. T. H. P.

New Colour Reaction of Quinine, Quinidine and Cupreine and its Application to the Determination of Quinine. J. A. Sanchez. (*J. Pharm. Chim.*, **1935**, **21**, 24–32.)—This method overcomes the difficulty of the lack of a selective solvent for quinine, and also avoids the complicated technique of the B.P. (1932) method. It is based on the fact that since quinine is the methyl ether of a phenolic alkaloid (cupreine), the latter may be produced by demethylation and coupled with a diazo-compound to form a coloured substance. The material (0·1 g.) is macerated with 0·2 g. of powdered lime and 2 ml. of water, the mixture is dried on the water-bath, and the residue is ground and heated for 10 minutes, with shaking, in a tube containing 5 ml. of boiling chloroform. The mixture is filtered, the residues being washed with chloroform, and the filtrate is evaporated, the new residue being warmed with 30 drops of 30 per cent. sulphuric acid and 2 ml. of water, and the mixture filtered when cold. The residue is washed with water until the total filtrate amounts to 10 ml. A tube containing 1 ml. of this filtrate is immersed in glycerin at 120° C. until no water remains, when the temperature is raised to 180° C. and maintained there for 5 minutes. The tube is cooled, and 2 ml. of water and 1 ml. of a fresh mixture of 10 ml. of a saturated solution of *p*-nitraniline in 1 per cent. sulphuric acid and 1 drop of 10 per cent. sodium nitrite solution are added. The mixture is shaken and made alkaline with 10 drops of 30 per cent. sodium hydroxide solution, after which it is acidified with 10 drops of 30 per cent. sulphuric acid and shaken with 2 ml. of 95 per cent. alcohol. The resulting orange colour is matched against that obtained from a solution of pure quinine sulphate in water (0·145 per cent. $C_{20}H_{24}N_2O_2,3H_2O$; 1 ml. ≡ 0·001 g. of quinine). The standards are prepared by adding to 10 tubes containing 0·1, 0·2, etc., to 1·0 ml. of quinine solution, respectively, 3 drops of the sulphuric acid and sufficient water to make 1 ml. These mixtures are then evaporated on a glycerin-bath and the colour is produced as described above. If a tincture is to be tested, 1 ml. is mixed with 0·2 g. of lime and 10 drops of water, the mixture is evaporated, and the above procedure is followed; fluid extracts should first be diluted with alcohol. The method is also applicable to quinidine (after demethylation), and, if it is necessary to separate this compound from quinine, it may be precipitated by means of a solution of an alkali iodide from the residue obtained after evaporation of the chloroform. Cupreine is determined directly, *i.e.* without demethylation. J. G.

New Adulterant of Cocaine. E. Collard. (*J. Pharm. Chim.*, 1935, **127**, 57–60.)—A sample of cocaine, m.p. 94° C., was found to contain about 33 per cent. of an insoluble substance which, on heating, sublimed with partial decomposition and emitted the odour of benzoic acid. It proved to be ethyl *p*-amino benzoate (anaesthesine), which, according to the German Pharmacopoeia, melts at 90°–91° C., although a sample used for comparison had m.p. only 88° C. A solution of anaesthesine in dilute hydrochloric acid differs from one of cocaine in that it does not give a precipitate with iodine in potassium iodide solution, but resembles it in being precipitated by picric acid. If sufficiently dilute solutions are used and precipitation is brought about slowly, crystals shaped like palm leaves are produced in both cases, but the two picrates differ in appearance (illustrations are given); in stronger solutions the tufts of crystals are very similar. D. G. H.

Determination of Certain Local Anaesthetics derived from Amino-Alcohols. F. and J. Girault. (*J. Pharm. Chim.*, 1934, **126**, 584–586.)—The anaesthetic is determined by precipitating the amino alcohol base by ammonia, extracting with ether, and washing and shaking with excess of acid. The excess of acid is isolated and titrated in the presence of methyl red, and the quantity of anaesthetic is determined from the proportion of combined base found by difference. About 0·001 of the molecular wt. of the anaesthetic is weighed, and washed into a separating funnel with the smallest possible amount of water. Fifty ml. of ether are added, and then, after shaking, 0·5 ml. of ammonia (French off.), followed by 10 minutes' shaking. The water fraction is drawn off into another funnel, 30 ml. of ether added, and, after shaking as before, the water is withdrawn. The ammonia is removed from the united ethereal extracts by washing with water at least four times, using 10, 5, 5, and 5 ml. respectively, and 20 ml. of 0·1 *N* hydrochloric acid are added. After shaking for 10 minutes the aqueous acid layer is withdrawn, and the ethereal solution washed three times with 10, 5, and 5 ml. of water, and the washings are added to the acid. Ether is driven off by heating the acid solution, and the excess of acid is titrated. Detailed examples are given for stovaine, novocaine, and larocaine. D. G. H.

Carbohydrates of Tobacco and their Significance. C. Pyriki. (*Z. Unters. Lebensm.*, 1934, **68**, 554–566.)—Most of the tobaccos examined—of Oriental, overseas and German origin—contain below 0·5 per cent. of invertible sugar, the maximum found being 0·9 per cent. The tobacco extracts obtained contained large proportions of salts, and the sugars could not be isolated free from these.

By comparison of the optical activity with the reducing power, by examination of the phenylosazones, by the reaction with bromine, and by colour reactions, the sugars were, however, identified as dextrose and laevulose, the latter being in excess. Most of the Oriental tobaccos contained relatively large proportions of sugars, the better qualities showing from 5·5 to 13, and the poorer ones from 0 to 4 per cent. German and cigar tobaccos proved almost free from sugar. Oriental tobaccos rich in sugar contained comparatively little nicotine, and those with higher nicotine-contents smoked mild; the varieties with no or very little sugar were usually strong and bitter. The sugar-content had a marked influence on the acidity of the smoke from Oriental tobaccos, but is not regarded as the sole cause of the acid reaction. Near the stalk of the leaf the amount of sugar is greater than near the tip, and the distribution of nicotine in the leaf is related inversely to that of the sugar. The starch-content of the tobaccos examined varied from 1·1 to 8·3 per cent., and with Oriental tobaccos, those free from sugar contained but little starch. In general, the percentage of pentosans present ranged only from 3·8 to 4·9, but German tobaccos showed from 5·5 to 6·4 per cent. No relationship was observable between starch- and pentosan-contents and the quality of the tobacco. T. H. P.

Colorimetric Test for Quillaia Saponin. J. Rae. (*Pharm. J.*, 1935, **134**, 59.)—If 10 ml. of a 1 per cent. solution of quillaia saponin are treated in a Nessler glass with 1 ml. of 10 per cent. sodium nitrite solution and 2 drops of sulphuric acid, followed, after 30 seconds, by 20 ml. of *N* sodium carbonate solution (a few drops of ether being used to prevent frothing), a yellow colour, reaching its maximum intensity in 5 minutes, is produced, and the depth of colour is proportional to the amount of saponin present. The reaction was positive with 5 different samples of quillaia bark saponin, but negative with a sample of unknown origin and with digitonin, which were also negative to Mitchell's test (ANALYST, 1926, **51**, 181). So far, the test is not directly applicable to quillaia bark, owing to the interference of substances extracted with the saponin, and preparations of senega give a wine-red colour, but saponin used as a denaturant in toilet and perfumery preparations made with industrial spirit may be quantitatively determined. One per cent. of saponin was added to petroleum emulsion, and the amount determined colorimetrically was 0·92 per cent. Phenols and other substances reacting with the reagents used must be absent. D. G. H.

Saponin from Soya-bean. R. C. Burrell and E. D. Walter. (*J. Biol. Chem.*, 1935, **108**, 55–60.)—The saponin was extracted by refluxing 4 kg. of finely ground soya-bean meal with 5 l. of 80 per cent. alcohol, at 50–70° C., in a specially-made copper boiler. From the extract the solvent was removed by distillation, and the heavy liquid remaining was dialysed in an electro-dialyser with 200 ml. of water at 100 volts for 24 hours. The supernatant liquid was siphoned off, and the precipitate was collected on a filter and dried on a steam-bath. The dried residue was extracted with ether in a Pickel extractor for 24 hours. The residue from the extraction was dissolved in 70 per cent. alcohol, and the solution was clarified with "Darco," and evaporated to about half its volume. From this solution, crystals of the saponin separated. When first removed from the mother liquor they had the form of micro-rosettes, but, after being dried over sulphuric acid they became very thin plates. These crystals melted at 220–225° C. with decomposition, were soluble in methyl and ethyl alcohols, in acetone and in caustic alkali, giving solutions which foamed on shaking. An average analysis was C = 59·24 per cent. and H = 8·52 per cent. with a molecular equivalent of 769. The saponin on long-continued hydrolysis yielded a sapogenin, which probably contained a terpene grouping, galactose and possibly rhamnose. It is suggested that it is probable that several of the recently reported saponins from soya-bean are identical, and also that the hydroxy acid reported by Muramatsa (*Bull. Imp. Coll. Agric. and Forestry*, 1924, **7**, 31) was a difficultly hydrolysable, insoluble, acid saponin. S. G. S.

Sodium Dinitrophenate. J. C. Bird, Z. Panciera and E. G. E. Shafer. (*Amer. J. Pharm.*, 1934, **106**, 462–466.)—To determine the water of crystallisation in sodium dinitrophenate, 1 to 2 g. of the sample are heated in an air-oven at 160–170° C., for at least 2 hours, or until constant in weight. Percentage loss was found to be 8·05 per cent., corresponding with 1 H_2O. Sodium may be determined by applying heat in such a way that the entire surface of the crucible is heated gently and uniformly, otherwise simple ignition invariably results in explosion. Methods of reduction and precipitation involve complicated procedures. The sample taken for the water determination may also be used for the determination of sodium (provided that a platinum crucible or dish is used), and the dehydrated material is moistened with about 5 ml. of concentrated sulphuric acid, and placed in a "chimney heater." The temperature is gradually raised until the material is charred and there is no further tendency to "creep," after which heating is continued over a small open flame, and, finally, the material is strongly ignited until a pinkish-white residue is obtained. This is cooled and moistened with sulphuric acid, and, after further heating and cooling, the anhydrous sodium sulphate is weighed. An average of 10·29 per cent. of sodium was found (the calculated figure being 10·27), allowing for one mol. of water. The "chimney heater" used was made from a 5-lb. ether can, with the top removed, a nichrome triangle to support the crucible being inserted about midway up by running the ends through holes in the sides of the can. When heated, yellow sodium dinitrophenate becomes increasingly red, fusing to a deep purple or black mass; if heating is rapid, explosion follows immediately upon fusion. If heated slowly, the material appears to "boil," and explosion eventually follows with even greater violence. D. G. H.

Two New Crystalline Principles from Indian Species of Artemisia (from the Laboratories of Messrs. T. and H. Smith, Ltd.). (*Pharm. J.*, 1935, **134**, 3–5.)—Two new crystalline principles, distinct from santonin or artemisin, have been found in species of *Artemisia* collected on the N.W. frontier of India. These were isolated in the ordinary course of an assay for santonin and the names pseudo-santonin and *k*-santonin were suggested. Clemo (*J. Chem. Soc.*, 1934, 1343) has found that *k*-santonin is a laevo-isomer of santonin, but pseudo-santonin has not yet had its constitution determined. The following table shows the relationship existing between these compounds:

	True santonin	*k*-santonin	Pseudo-santonin	Artemisin
M.P.	172° C.	216–218° C.	184–186° C.	200° C.
Specific rotation	−172·5° C.	−140° C.	−172·5° C.	−84·3° C.
Sensitivity to light	Very sensitive	Less sensitive	Insensitive	Less than santonin
Alcoholic potash	Carmine-red	Pale carmine-red	Brownish-yellow	Pale carmine-red
Sulphuric acid conc.	No colour	No colour	Dark brown	No colour
Solubility in:				
Alcohol (90 per cent.)	1–50	1–116	1–15	—
Ether (0·720)	1–140	1–625	1–312	—
Chloroform	1–2·5	1–4·2	1–4·2	Forms a compound
Boiling water	1–416	1–590	1–45	1–60
Cold water	Almost insoluble	Almost insoluble	1–300	—

S. G. S.

Oxidation of Rotenone by Copper in an Alkaline Medium. R. M. Whittaker and I. Glickmann. (*Rec. Trav. Chim. Pays-Bas*, 1934, **53**, 1145–1150.)—This reaction of rotenone serves for its determination in alcoholic solution, but is not found adaptable to the assay of plant material for rotenone-content. With derris-root extracts, for example, other reducing substances present cause high results. It may, however, be possible to establish an arbitrary relationship between the reducing values in terms of dextrose and the toxic powers of such extracts. The reagents required are: (i) Aldehyde-free alcohol. (ii) Alkaline copper solution: Dissolve 2·5 g. of pure copper sulphate ($+5H_2O$) in about 100 ml. of warm water, cool, add a solution of 5 g. of pure sodium potassium tartrate and 7·5 g. of sodium hydroxide in 100 ml. of water, and make up to 500 ml. This should not be used after it is three days old. (iii) Folin's reagent: Dissolve 150 g. of sodium molybdate in 300 ml. of water, filter the solution through a small quantitative paper and wash the residue with about 75 ml. of water, add 0·1 to 0·2 ml. of bromine and shake till this is dissolved. After an hour, add, with shaking, 225 ml. of 85 per cent. phosphoric acid, and then 150 ml. of dilute sulphuric acid (1+3). Remove the free bromine by means of a current of air, add 75 ml. of 99 per cent. acetic acid, and make up to 1 litre. (iv) Dissolve 1 g. of pure, anhydrous dextrose in water, add 40 ml. of aldehyde-free alcohol and dilute to 200 ml. with water; 10 ml. of this stock solution and 210 ml. of aldehyde-free alcohol are made up to 250 ml. with water.

Standard rotenone solutions are prepared from the commercial product, first recrystallised several times from alcohol, dried, and stored over calcium chloride. Ten ml. of the standard rotenone solution are treated with 6 ml. of reagent (ii) in a test-tube, which is kept for 45 minutes in a bath at 78° C., and then for 3 minutes in a bath at 20° C. Ten ml. of reagent (iii) are added and, after 3 minutes, the solution is diluted to 90 ml. with water, filtered through a thick asbestos pad in a Gooch crucible, and diluted to 100 ml. This solution is at once compared colorimetrically with the solution obtained from 10 ml. of the diluted dextrose standard in a similar manner, except that this need not be filtered.

The relation between the amounts of rotenone and dextrose is found to be: $Y = 0{\cdot}6195 - 0{\cdot}006858X + 0{\cdot}008371X^2$, Y and X being the numbers of mg. of dextrose and rotenone, respectively. Results accurate to about 0·2 per cent. are thus obtainable. T. H. P.

Organic

Reactions and Reagents for the Detection of Organic Compounds. III. E. Eegriwe. (*Z. anal. Chem.*, 1935, **100**, 31–36; *cf.* ANALYST, 1932, **57**, 584.)—*Glycerol.*—Two drops of an aqueous solution to be tested for glycerol are placed in a test-tube, which is then filled with bromine vapour, covered with a small funnel with sealed-up end, and heated for 10 minutes in a water-bath at 85° to 90° C., and, after removal of the funnel, for 10 to 15 minutes longer. Any residual trace of bromine is rendered ineffective by addition of a small crystal of sodium sulphite. A little concentrated sulphuric acid is poured down the wall of the inclined tube, which is meanwhile, and during the subsequent mixing, kept cool under the tap. Further sulphuric acid is added to give a total volume of 2 to 3 ml., a little solid *m*-hydroxybenzoic acid is introduced, and the tube is swirled and then left for 10 to 15 minutes in a water-bath at 65° to 70° C. The presence of glycerol is shown by the appearance of a green fluorescence, which appears even with one drop of solution containing 0·005 mg. of glycerol. The fluorescence obtained with 0·024 mg. of glycerol is apparent in presence of twice as much sucrose or six times as much glycol or dextrose; laevulose has a somewhat greater disturbing action.

Allyl Alcohol.—This alcohol (0·003 mg.), which also gives dihydroxyacetone on oxidation, may likewise be detected as described above.

Glyoxylic Acid.—One drop of the aqueous solution is mixed in a test-tube with a little solid pyrogallol-4-carboxylic acid, and one or two drops of concentrated sulphuric acid are poured down the wall of the inclined tube, which is kept cool. The volume is made up to 0·5 to 0·75 ml. with the sulphuric acid, and the tube is heated for 30 minutes in a bath at 40° C. A blue colour is formed with as little as 0·001 mg. of glyoxylic acid in one drop of the aqueous solution.

Oxalic Acid.—As this is reducible to glyoxylic acid, the previous test may be applied. To one drop of oxalic acid solution (or one drop of a solution of calcium oxalate in dilute sulphuric acid) in dilute sulphuric acid is added a small quantity of powdered magnesium, and when this has dissolved the pyrogallolcarboxylic acid reaction is used. The blue colour appears with 0·02 mg. of oxalic acid in one drop of solution. This reaction is not given by the near homologues of oxalic acid or by pyruvic, laevulinic, or acetonedicarboxylic acid, but is shown by mesoxalic (not precipitable by calcium sulphate solution) and dihydroxytartaric acids. T. H. P.

Action of Nessler's Reagent on some Ketonic Alcohols and Ketonic Acids. G. Schuster. (*J. Pharm. Chim.*, 1935, **21**, 32–43.)—The following results were obtained:—*a-Ketonic Alcohols.*—Dimethylacetol: oxidation is complete after 15 minutes, the oxygen consumed being equivalent to 2 atoms of iodine. Dihydroxyacetone: 90 minutes, 8 atoms. Propionin: 4 hours for total oxidation (*i.e.* of the secondary alcohol and of the diacetone), 4 atoms. Butyroin, 90 minutes.

Iso-butyroin, rapid oxidation on the water-bath, 4 atoms. Capronoin, 90 minutes, 4 atoms. Hydroxyacetophenone (in methyl alcohol containing hydrochloric acid), 15 minutes, 8 atoms. Benzoin (in methyl alcohol), 15 minutes below 10° C.; dibenzyl is produced. *β- and γ-Ketonic Alcohols.*—Chloralacetophenone, chloralpropanone and benzoylacetone are not oxidised, but a green precipitate of mercurous salts is formed and is accompanied by what is probably a product of the transformation from the ketonic to the enolic form, with the occurrence of a double-linkage. Acetonylacetone produced a yellow precipitate similar to that obtained with all the ketones, but there was no evidence of reduction of the reagent. *a-Diacetones and a-Ketonic Acids.*—Diacetyl and dibenzyl are oxidised slowly at 20° C., but dibutyryl is oxidised only on the water-bath, and then very slowly. Pyruvic acid, ethyl-phenylglyoxylate and ethyl-aceto-acetate are not oxidised, although the yellow precipitate is produced. Nessler's reagent may therefore be used to determine the ă-ketonic alcohols (if these are allowed to react at the temperature of the water-bath), the final procedure being to acidify the mixture with hydrochloric acid, and to add 20 ml. of a 0·1 *N* solution of iodine, the excess of which is titrated with 0·1 *N* sodium thiosulphate solution (*cf.* Bouveault, *id.*, 1906, **35**, 629; Bougault and Gros, ANALYST, 1922, **47**, 405). Methods of preparation and reaction-rate data are given in each case. J. G.

Detection of Diazonium Salts and Primary Amines by means of Resorufin. H. Eichler. (*Z. anal. Chem.*, 1934, **99**, 348–350.)—To test for diazonium salts, the filtered, slightly acid liquid is added to 5 to 10 ml. of water rendered distinctly fluorescent by adding a solution of 0·2 g. of resorufin and 0·2 g. of sodium carbonate in 100 ml. of water. The acid liquid is then made alkaline with sodium carbonate. If a diazonium salt is present, the liquid becomes brown and non-fluorescent; otherwise, the red fluorescence of the resorufin persists unchanged. In some cases formation of the colouring matter with the resorufin proceeds slowly, addition of ammonium chloride or sulphate or replacement of the sodium carbonate by the bicarbonate or ammonium carbonate then being advisable. Diazotised toluidines are best detected in ammoniacal solution. In all cases the reaction is hastened by heating the liquid. Any metal salts present must be removed by sodium acetate or a small quantity of sodium carbonate before the above test is applied. Diazotates are first treated with dilute hydrochloric acid to convert them into the corresponding diazonium salts. Under the above conditions, fluorescein forms sparingly soluble, non-fluorescing dyes only with certain diazonium salts, *e.g.* those of *p*-toluidine. This behaviour may be utilised to detect and identify such amines or diazonium salts in presence of substances which yield no dyes with fluorescein.

Nitrous acid or nitrites may be detected by the author's Magdala red method (ANALYST, 1934, **59**, 303). Diazonium salts should first be destroyed by gently heating the faintly acid liquid, where possible in presence of added copper salt or alcohol. Any mineral acid present should be annulled by addition of sodium acetate.

To detect primary amino groups in aromatic compounds, the hydrochloric acid solution is diazotised by sodium nitrite at 0° to 10° C., and the resorufin test then applied to the diazonium chloride formed. Prior to diazotisation, difficultly soluble aminocarboxylic acids may be obtained in finely divided form by dissolving them in alkali and precipitating with hydrochloric acid. Primary amino groups in readily diazotised organic dyestuffs may be detected similarly. Dyestuffs of low solubility may be dissolved in concentrated sulphuric or glacial acetic acid and precipitated in finely divided form with ice-water. Dyestuffs on fibres are extracted by means of water, glacial acetic acid, dilute acids or sodium carbonate solution. T. H. P.

Brazilian "Cedro" Wood Oil. F. W. Freise. (*Perf. and Ess. Oil Record*, 1935, **26**, 11–12.)—Brazilian "Cedro" wood yielding essential oil may be derived from the trees of the N.O. *Meliaceae*, genus *Cedrela*; *C. odorata*; *C. angustifolia*, D.C., *C. montana* Karst., *C. macrocarpa* Ducke, *C. fissilis* Vell., *C. australis* Juss., St. Hil., and *C. glaziovii* D.C., the frequency of their occurrence being in the order cited. The roots of old and very strong individual trees contain from 2·0 to 3·5 per cent., and yield 1·6 to 3·2 per cent. of oil, whereas chips contain 0·8 to 1·8 per cent., and yield 0·5 to 1·4 per cent. of oil. Sawdust yields only 0·08 to 0·2 per cent., and leaves when fresh may give 0·03 to 0·05 per cent. of oil. Exceptionally, however, the yields may be considerably higher. The fruit capsules of *C. macrocarpa* and *C. glaziovii*, in the fresh half-green state, contained 0·04 to 0·085 per cent. of oil, but practically none when ripe; the seeds contain only a very small proportion of a fixed oil. Crude commercial "Cedro" wood oil, which is extracted with steam, is of a bluish colour, but so far no such colour has been observed in any oils obtained in the laboratory. The crude oil has a sp.gr. at 20° C. of 0·900 to 0·965°, whilst the optical rotation, which is positive or negative, ranges from +6° 35′ to −4° 25′. Solubility is complete in 6 vols. of 90 per cent. alcohol. Figures obtained for various samples extracted in the laboratory were as follows:

Original plant and part employed	Yield on dried material Per Cent.	Sp.gr. 20°/4° C.	α^{20°	$n_D^{20^\circ}$	Acid value	Ester value	Main constituents
C. fissilis, young roots	3·37	0·933	− 11° 15′	1·4985	1·55	26·5	Cadinene, cineol, α-pinene
,, woodchips	2·86	0·922	− 5° 35′	1·5055	2·51	38·3	ditto; pinene in traces
,, leaves	0·13	0·896	− 2° 50′	1·4826	1·82	41·5	Camphene
C. odorata, fresh sawdust	0·22	0·911	−13° 30′	1·5210	Not determined	N.D.	
,, raspings	0·31	0·921	− 9° 30′	1·4955	1·93	38·8	Cadinene, borneol
C. montana, roots	2·72	0·944	−14° 10′	1·4474	2·11	44·4	
,, shavings	1·88	0·931	Not determined		3·13	38·3	Cadinene, α-pinene
,, old chips	0·92	0·915	Not determined		2·83	44·5	Pinene, cineol in traces
C. macrocarpa, capsules	0·09	0·927	− 4° 35′	1·5228	1·06	26·8	Camphene, α-pinene

All these oils were soluble in 4 vols. of 90 per cent. alcohol, and were of a clear yellow colour, except that the oil from *C. odorata* gave a slightly opalescent alcoholic solution, and the oil from leaves and capsules had a greenish tinge. D. G. H.

Biochemical

"Digestibility" of Common Foodstuffs as Determined by Radiography. W. C. D. Maile and K. J. L. Scott. (*Lancet*, 1935, 21–23.)—X-ray screening methods were applied, 1 ounce of "barium," mixed either with the food or with a little water which was taken with the food, being used. It was found that an ordinary meal leaves the stomach in about 4 hours, and a large meal in 5 hours; if the meal contains much fat (especially as butter or cream) it may be retained much longer, even if the quantity is not unduly large. Concentrated carbohydrates (*e.g.* sugar) leave the stomach more rapidly than natural carbohydrates (*e.g.* banana or potato). With some foods (*e.g.* milk) cooking shortens the time of stomach digestion, but with others (*e.g.* eggs) the time is lengthened. The period of stomach digestion of different foods cannot be taken as a measure of their "digestibility," and, since the sensation of hunger does not necessarily result from an empty stomach, there is no support for the view that it is due to vigorous peristaltic contractions of the stomach. In general the figures indicate a rather longer emptying-rate than "digestibility" tables based on tube experiments (*cf.* Rehfuss and others, *Amer. J. Physiol.*, 1919, **49**, 174, 204, 222, 254; 1920, **51**, 332; 1920, **52**, 1, 28, 248). This may be explained by the fact that barium delays the emptying of the stomach or is left as a coating to the lower part of the greater curvature after the food has passed through the pylorus; a more likely explanation is that the presence of a Rehfuss tube in the stomach acts as an irritant, and causes exaggerated peristalsis.

J. G.

Influence of Freezing Temperatures on Haddock's Muscle. G. A. Reay. (*J. Soc. Chem. Ind.*, 1934, **53**, 413–416T.)—The freezing and thawing of muscle are accompanied by a partial irreversible physico-chemical breakdown of muscle-plasm, with increased insolubility of the proteins. The process is also associated with an increase in the amount of fluid that can be easily expressed from the muscle (termed "drip"). Minced haddock muscle (149 g.) was packed into circular tinned cans (9·6 × 2 cm.), and the ends were hermetically sealed on. After freezing and thawing, the ends were removed and pads of filter paper were applied to the flat surfaces, close contact being assured by means of a lead plate weighing 0·5 lb. placed on top of the paper. After standing 17 hours at 5° C. the cake of muscle was removed, and the loss in weight determined. The maximum formation of "drip" occurred between −1° and −3° C., and the quicker the freezing and thawing the less the drip. The amount of the various kinds of change brought about by freezing is closely dependent on the time spent within the zone of maximum change, −1° to −5° C., during any complete temperature time-cycle. The increasing insolubility of the proteins, brought about as a result of freezing and thawing, is not held to be the cause of the "drip" which develops from one hour's exposure to temperatures in the critical range, −1° to −5° C. (accounting for one-third of the total "drip" obtainable by the longest exposure at the temperature range, whereas measurable denaturation does not occur until after 7 hours' exposure). The secondary slow increase in "drip" with a period of exposure up to 10 days or so may, however, be attributable to the corresponding denaturation development. The initial rapid formation of "drip" is regarded as due to the structural changes brought about by the formation of ice. D. G. H.

Use of Tartrazine in the Determination of Chlorides in Biological Material. W. R. Fearon and W. A. Gillespie. (*Biochem. J.*, 1934, **28**, 1629–1630.)—Chlorides may be determined in protein-free solutions, such as sea-water and normal urine, by mixing 10 ml. of 0·1 *N* silver nitrate solution with five drops of pure nitric acid and 2 to 5 drops of 0·5 per cent. aqueous tartrazine solution. The solution under analysis is used to titrate this mixture, 0·1 to 0·5 ml. being added at a time, with shaking. The precipitate is at first buff in a colourless solution. The end-point occurs when the precipitate becomes white and the solution greenish-yellow. If only a small quantity of liquid is available, one ml. may be added to the acid solution of silver nitrate and indicator, and the mixture titrated with 0·1 *N* hydrochloric acid. Proteins affect the solution colour and, if they are present, the second method should be used. Proteins also affect the silver nitrate solution by altering its chloride value, and, if possible, should be removed by coagulation or precipitation. S. G. S.

Influence of Antiseptics on Yeast Autolysis. H. Haehn and H. Leopold. (*J. Inst. Brewing*, 1935, **41**, 44.)—If yeast is incubated at 50° to 52° C., no development of foreign organisms takes place, even in the absence of antiseptics. At this temperature autolysis occurs, the whole liquefying in 24 hours. This was allowed to proceed for 21 days, both alone and with 5 per cent. of toluene, chloroform, and ethyl acetate, respectively. The *p*H value, titratable acidity, inorganic phosphates, total soluble nitrogen, and formol and ammoniacal nitrogen were determined at intervals, the results indicating that proteolysis and the formation of acid products and inorganic phosphates are retarded more by chloroform and ethyl acetate than by toluene, but that the last has a retarding effect on the increase in titratable acidity and the fall of the *p*H value. Toluene has but a slight effect on proteolysis. Ethyl acetate is hydrolysed to some extent, but the acetic acid formed also retards autolysis. S. G. S.

Detection of Volutin in the Living Yeast Cell by means of Neutral Red. L. Heucke and W. Henneberg. (*Woch. Brau.*, 1934, **90**, 425 ; *J. Inst. Brewing*, 1935, **41**, 43.)—The volutin in yeasts, moulds and bacteria was rendered visible by staining with neutral red. One drop of a 0·001 per cent. aqueous solution of neutral red was mixed with a drop of yeast suspension on the microscope slide. Dead cells were stained uniformly throughout, but in the living cells the colour was absorbed by the volutin globules, which were situated both in the vacuole and in the protoplasm. The vacuoles (but not the protoplasm) gradually became pale red and then dark red. Those cells having red vacuoles or volutin died after a short time. When specimens of living organisms prepared by this method were compared with Löffler-blue formaldehyde preparations, cells from a fresh fermentation being used for both, it was found that in the living preparations the volutin was in the form of one large globule (resting form), whereas in the other preparation the volutin consisted of many small globules (working form). Yeast from old agar cultures gave the resting form by both methods. When living yeast spores were stained with neutral red, one volutin globule in each spore was rendered visible. Wort-agar containing 0·001 to 0·005 per cent. of neutral red was a satisfactory medium for the growth of yeast, even though many cells contained stained volutin; but the presence of the dye in a concentration of 0·01 per cent. inhibited the growth of beer yeast. S. G. S.

Determination of Sodium in Human Red Blood Cells. F. W. Oberst. (*J. Biol. Chem.*, 1935, **108**, 153–160.)—The sodium-content of red blood cells was determined by drawing venous blood into a 50-ml. centrifuge tube, treating it with heparin (0·1 ml. of a solution of 75 mg. of heparin in 5 ml. of water per 5 ml. of blood and evaporating off the water), and centrifuging for 30 minutes, at 3000 R.P.M. The plasma with 0·5 ml. of cells was removed by suction and the remaining cells thoroughly mixed. Some cells were analysed unwashed, and others were washed with isotonic potassium chloride solution, or with sodium-free dialysed serum made isotonic with potassium salts and equilibrated with approximately 40 mm. of carbon dioxide. Protein was removed either by treatment with trichloroacetic acid or by ashing, and phosphates were removed by means of powdered calcium hydroxide. The sodium-content was determined colorimetrically by the sodium-zinc-uranyl acetate method. Tables are given showing the effect of the various treatments on the sodium-content, the average value of which was 16·6 mg., with a range of from 14·1 mg. to 20·3 mg., per 100 g. of cells. S. G. S.

Method for the Determination of Sucrase Activity. J. B. Sumner and S. F. Howell. (*J. Biol. Chem.*, 1935, **108**, 51.)—The definition, by Willstätter, of a unit of sucrase activity based on the time necessary for the rotation of a sucrose solution to be reduced to 0, is criticised, and a new definition and method of determination are suggested. The suggested unit is based on the number of mg. of invert sugar formed in 5 minutes at 20° C., at *p*H 4·5. This may be determined by placing 5 ml. of 6·5 per cent. sucrose in an acetate buffer solution in a test-tube and heating the mixture to 20° C. in a thermostat. One ml. of sucrase solution or yeast suspension at 20° C. is added from a Folin–Ostwald pipette which delivers rapidly, and the solutions are mixed and kept in the bath for 5 minutes, after which 5 ml. of 0·1 *N* sodium hydroxide are added. The invert sugar in the mixed liquids is determined in 1 ml. by the dinitrosalicylic acid method (*J. Biol. Chem.*, 1925, **65**, 393), a 1 mg. glucose standard being used. The number of mg. of invert sugar, multiplied by 11, gives the number of sucrase units per ml. of enzyme solution. If more than 1 mg. or less than 0·5 mg. of invert sugar is found per ml., the analysis must be repeated with an adjusted amount of sucrase solution or a longer or shorter time for digestion. Yeast preparations containing sugar must be washed before being tested. The sucrose and acetate buffer solution is prepared by mixing 43 ml. of *N* sodium acetate solution with 57 ml. of *N* acetic acid and diluting to 1 l. with water redistilled from glass. If 6·5 g. of sucrose are dissolved in 96 ml. of this solution and a few drops of toluene added, the result will be a product which has *p*H 4·5, and will remain serviceable for 3 days. Glucose is used for the sugar standard because it gives the same reducing value as invert sugar by the dinitrosalicylic acid method. S. G. S.

Research on Vitamin *A* in Animal and Plant Cells. P. Joyet-Lavergne. (*Compt. rend.*, 1935, **200**, 346.)—The well-known antimony trichloride reaction for vitamin *A* has been applied to living cells from animal and vegetable sources. In sporozoite forms the blue colour was localised in the elements of the chondriome. In all cells examined the chondriome gives the blue colour, but the intensity of this may vary from cell to cell. Hepatic cells give a strong colour, and the salivary gland cells of *Chironomus* gave a poor colour. Between these extremes a wide range of intensity was obtained. Studies on species of *Coccidia* and *Gregarina* revealed the fact that the chondriome conserves its vitamin *A* even throughout the varying morphology of the animal's life cycle. Vitamin *A* was also found in the cytoplasm (outside the chondriome) in the liver cells of certain salt-water fish. No vitamin *A* was found in the nucleus unless a nucleole was present. It is suggested that in plant cells the reaction is given by carotene, $C_{40}H_{56}$, but that in animal cells it is the true vitamin, $C_{20}H_{30}O$, that reacts. S. G. S.

Influence of the Solvent on the Biological Assay of Vitamin *A*. K. C. Lathbury and G. N. Greenwood. (*Biochem. J.*, 1934, **28**, 1665–1673.)—In the biological assay of carotene and vitamin *A* concentrates the values found may vary with the oil used, and the results may be very contradictory. Results of experiments on various batches of coconut and arachis oils, described in detail, show that the suitability of a particular oil can be determined only biologically, for the variation is independent of the stability of the dissolved substance in the oil. The carotene or vitamin *A* had not lost its activity as shown by colour tests, and yet the biological results were very variable. This is thought to be due to an unknown factor in certain oils. The addition of quinol will not render an inferior oil suitable for biological assay. S. G. S.

Properties of Carotenes from certain Roots and Leaves at Various Stages of Development. G. MacKinney. (*J. Biol. Chem.*, 1935, **108**, 45–49.)—Carotene was isolated in crystalline form, from carrot roots, the leaves of English ivy (*Hedera helix*), and coastal redwood (*Sequoia sempervirens*) at various stages of development. It was found that both α- and β-components may be present together, and that the ratio $\alpha : \beta$ showed no significant change with the degree of maturity of the organ containing them. The mixed crystals gave optical rotations $\alpha^{20°}_{667\cdot 8}$ from +59° to +97° in benzene, and melted at 162° to 174·6° C. according to the proportion of each component present. S. G. S.

Concentration of Vitamin *G* (B_2) by Adsorption and Elution from Fuller's Earth. S. Lepkovsky, W. Popper and H. M. Evans. (*J. Biol. Chem.*, 1935, **108**, 257–265.)—Vitamin B_2 derived from fresh liver extracts is capable of being adsorbed on fuller's earth in neutral or strongly acid solutions, such adsorption being complete in 10 minutes (above *p*H 8·0 the adsorption is poor). The adsorbates may be eluted with diluted diethylamine (10 to 50 per cent. in aqueous solution) or diluted caustic soda solution (0·2 per cent. in water), with little loss of activity. S. G. S.

Erratum.—Dialysis of Milk. L. H. Lampitt and J. H. Bushill, abst. ANALYST, 1934, **59**, p. 828, line 12, *for* "250 ml." *read* "25 ml."

Inorganic

Solubility of Lead Sulphate in Water and Aqueous Sulphuric Acid. H. D. Crockford and D. J. Brawley. (*J. Amer. Chem. Soc.*, **1934, 56,** 2600–2601.)—The solubility of lead sulphate has been determined in pure water, and in sulphuric acid solutions containing up to 80 per cent. of the acid, at 0°, 25°, 35° and 50° C., with the following results:

Sulphuric acid Per cent. by vol.	Lead sulphate, p.p.m.			
	0° C.	25° C.	35° C.	50° C.
0·00	33·0	44·5	49·7	57·7
0·005	8·0	10·0	11·0	24·0
0·01	7·0	8·0	10·0	21·0
0·02	6·4	7·0	8·0	18·0
0·05	5·2	6·0	6·6	15·0
0·10	4·6	5·2	5·6	13·0
0·20	3·4	3·8	4·5	12·0
0·50	2·0	2·5	4·3	11·5
1·00	1·8	2·2	4·2	11·3
5·00	1·6	2·0	4·0	10·3
10·00	1·2	1·6	3·8	9·6
20·00	0·5	1·2	2·8	8·0
30·00	0·4	1·2	2·0	4·6
40·00	0·4	1·2	1·8	2·8
50·00	0·4	1·2	1·8	2·8
60·00	0·4	1·2	2·0	2·8
70·00	1·2	1·8	2·4	3·0
75·00	2·8	3·0	3·8	6·6
80·00	6·5	11·5	24·0	42·0

For the determination of lead sulphate the following methods were used, (*a*) in *pure water*; the lead was precipitated as chromate and then titrated iodimetrically according to the method of Kolthoff and Rosenblum (*id.*, 1933, **55**, 2656); (*b*) in *acid solution* (lead concentration less than in pure water): the lead was precipitated as chromate in 100-ml. Nessler tubes, and the turbidity produced was compared with standards prepared as nearly like the unknowns as possible; this method was found suitable for determining 0·01 to 0·15 mg. of lead sulphate. The solid phase in equilibrium with the solutions was in all cases normal lead sulphate. S. G. C.

Volumetric Determination of Copper. E. Voyatzakis. (*Bull. Soc. Chim.*, **1934, 1,** 1356–1357.)—The process is a modification of Weil's method, in which cupric salt is reduced in hydrochloric acid solution by stannous chloride. The author replaces stannous chloride by potassium chlorostannite, a known quantity of which is added to the copper solution, the excess being titrated with iodine. The reducing agent is prepared from 15·5 g. of potassium chloride and 14·9 g. of stannous chloride, both in saturated solution, and a little hydrochloric acid. If necessary, the liquid is concentrated and left to cool during agitation. For the determination of copper, the sulphate solution freed from nitric acid is diluted with an equal bulk of strong hydrochloric acid in a flask, and the air is expelled by addition of sodium bicarbonate. An accurately weighed amount of powdered potassium chlorostannite is added, the cupric salt being immediately reduced to the cuprous state. The excess of stannous salt is at once titrated in the usual manner with iodine solution. If the concentration of copper in the solution is higher than 0·022 per cent., cuprous iodide is precipitated; hence the titration is carried out in dilute solution containing an equal volume of strong hydrochloric acid. Potassium chlorostannite is very stable and is easy to prepare in pure conditions (*cf.* Richardson, *Amer. Chem. J.*, 1892, **14**, 91). W. R. S.

Colorimetric Determination of Copper as Copper Sulphide. L. de Brouckère and S. Solowiejczyk. (*Bull. Soc. Chim. Belg.*, 1934, **43**, 597–625.)—In the absence of other metals which give coloured sulphides under the conditions employed, copper in solution may be determined by the addition of hydrogen sulphide water in the presence of 1 per cent. of gelatin as protective colloid. The method is applicable to solutions containing 0·003 to 0·03 g. of copper per l. and being 0·1 *N* to 0·5 *N* in sulphuric, hydrochloric, or nitric acid. The addition of the hydrogen sulphide water (2·5 ml. of saturated solution to 25 ml. of test solution) should be made simultaneously (using both hands) to the sample and to the standard solution of copper contained in colorimeter glasses, the colorimetric comparison being made after about 15 minutes with the aid of a Duboscq colorimeter. Results accurate within 1 per cent. were obtained in the presence of a large amount of the following salts added to the standard solution: alkali chlorides, nitrates and sulphates, the chlorides of magnesium, calcium and barium, and the sulphates of manganese, zinc and aluminium. Iron interferes. The results cited of test experiments occupy 19 tables. S. G. C.

Application of the Benzoate Method for the Separation of Iron, Aluminium, and Chromium in Qualitative Analysis. L. Lehrman and J. Kramer. (*J. Amer. Chem. Soc.*, 1934, **56**, 2648–2649.)—The recent method of Kolthoff, Stenger and Moskowitz (*id.*, 1934, **56**, 812; ANALYST, 1934, **59**, 435, 572) has been tested with regard to its use in qualitative analysis. Solutions containing 500 mg. of aluminium, tervalent chromium or tervalent iron, require respectively 90 ml., 60 ml. or 40 ml. of 10 per cent. ammonium benzoate reagent for complete precipitation after a 1-minute period of boiling. The bulk of the precipitate obtained with 500 mg. of the tervalent metals is rather large, but the precipitate can be contained in an 11-cm. filter paper, if filtered with the aid of suction. Two or three washings with 10 ml. of 5 per cent. ammonium nitrate solution remove practically all bivalent metal ions. One mg. of bivalent metal can be detected in the filtrate after precipitation of 500 mg. of any of the tervalent metals, alone or in combination. Before the filtrate is tested for the bivalent metals, the benzoic acid is removed by evaporating the acidified liquid until crystallisation begins, cooling, and filtering with the aid of suction. S. G. C.

Volumetric Determination of Niobium. J. A. Tschernichow and M. P. Karssajewskaja. (*Z. anal. Chem.*, 1934, **99**, 398–402.)—The authors have repeated the work of V. Schwarz (*Z. angew. Chem.*, 1933, **46**, 552), who reduced strongly acidified tartrate solutions by means of liquid zinc amalgam in complete absence of air; the reduced niobium compound was re-oxidised with ferric chloride, and the excess of ferric salt titrated with titanous chloride. Schwarz claims to have obtained concordant stoichiometric results, which the authors were quite unable to reproduce; the results of their 26 published tests differ too much even for the calculation of an empirical factor. They conclude that Schwarz has not solved the problem of the volumetric determination of niobium, and they concur with Schoeller and Waterhouse (ANALYST, 1924, **49**, 215) in considering oxidimetric methods for niobium unreliable. W. R. S.

Determination of Molybdenum as Silver Molybdate. L. W. McCay. (*J. Amer. Chem. Soc.*, 1934, **56**, 2548–2549.)—The solubility of silver molybdate in water is 0·044 g. per l. (25° C.), but when a moderate amount of silver nitrate is present in the water, the solubility is practically nil. The following method was employed for the determination of molybdenum in alkali molybdates, the element being precipitated and weighed as silver molybdate:—The solution (150 ml.) is acidified with sulphuric acid, methyl orange being used as indicator; 1 g. of sodium acetate is added, the solution is heated to boiling, and silver nitrate is added; the liquid is allowed to cool, and is stirred from time to time while cooling. The precipitate of silver molybdate is yellowish-white and curdy. It is filtered off on an asbestos filter with the aid of suction, and washed seven or eight times with 4 to 5-ml. quantities of silver nitrate solution (0·5 per cent.), the silver nitrate being finally removed by washing three times with 5-ml. quantities of alcohol (96 per cent.). It is dried at 110° C., then heated at 250° C., to remove the last traces of water, and weighed as Ag_2MoO_4. During the drying the precipitate changes in colour through pink to purple. Various samples of ammonium molybdate gave results in close agreement with the ignition method. The method is stated to be easier and more rapid than the mercurous molybdate and lead molybdate precipitation methods. S. G. C.

Volumetric Determination of Potassium by the Cobaltinitrite Method. C. S. Piper. (*J. Soc. Chem. Ind.*, 1934, **53**, 392–396T.)—As a result of a study of the method, the following technique has been evolved, yielding results in close agreement with the theoretical with 0·1 to 50 mg. of potassium oxide. The solution is evaporated to dryness. After cooling, 1·5 ml. of glacial acetic acid and 10 ml. of saturated sodium chloride solution are added, followed, after 5 to 10 minutes, by 5 ml. of sodium nitrite solution (35 per cent.). The liquid is stirred until all soluble matter is dissolved. After 5 to 10 minutes, but not longer, 5 ml. of cobalt nitrate solution (20 per cent.) are added rapidly (in less than 2 seconds), with stirring, from a burette with a large jet. The liquid is stirred for 40 to 60 seconds and kept overnight. The precipitate is filtered off in a Gooch crucible with an asbestos filter, or a crucible of sintered glass (G4) or unglazed porcelain, and washed either (*a*) 5 times with 10-ml. portions of freshly-prepared approx. saturated solution of potassium cobaltinitrite (this solution does not keep for more than about 30 minutes), or (*b*) 3 times with 10-ml. portions of 35 per cent. alcohol, then 3 times with 3-ml. portions of cold water. The crucible and precipitate are placed in 150 ml. of water to which have been added 5 ml. of concentrated sulphuric acid and a volume of standard permanganate solution (0·05 *N* or 0·02 *N*) about 5 ml. in excess of what the precipitate is likely to consume; the liquid is heated just to boiling and removed from the source of heat for 5 minutes; standard oxalic acid solution in slight excess is added, and the excess is back-titrated with standard permanganate solution. Eleven equivalents of oxygen are required for the oxidation of the cobaltinitrite molecule. The result is calculated with the aid of the empirical equation established by the author's work: K_2O (mg.) = permanganate value × 0·354 + (permanganate value)^2 × 0·00034; the "permanganate value" is the number of ml. of 0·05 *N* permanganate solution required in the titration. The composition of the precipitate was found by analysis to correspond with the formula $M_2Co(NO_2)_6$, where *M* represents *e.g.* sodium and potassium. The ratio of potassium to sodium varies according to the amount of potassium being determined, the amount and nature of the precipitating reagent, the amount of sodium salts present, and the temperature of precipitation. These variables are taken into account in the method of calculation adopted. Calcium, magnesium, iron, aluminium, sulphate, chloride, and phosphate do not interfere with the precipitation. S. G. C.

Microchemical

Volumetric Determination of Calcium in Serum. F. Rappaport and D. Rappaport. (*Mikrochem.*, 1934, **15**, 107–110.)—The calcium is precipitated from the serum (0·2 ml.) with ammonium oxalate, the precipitate is washed and dissolved in dilute sulphuric acid, and the liberated oxalic acid is oxidised with a measured quantity of 0·001 *N* ceric sulphate solution. The excess of cerium sulphate is then determined by titration with 0·001 *N* thiosulphate solution. *Reagents.*—(i) Cold saturated ammonium oxalate solution; (ii) 4 *N* sulphuric acid; (iii) a solution of 2 ml. of concentrated ammonia diluted to 100 ml.; (iv) cerium sulphate solution (0·001 *N*), made by dissolving 1 g. of the finely-powdered salt in 100 ml. of water containing 30 ml. of concentrated sulphuric acid, and diluting the solution to about 750 ml. (This solution is standardised against 0·001 *N* thiosulphate solution, diluted to approximately the correct volume, and again standardised; the solution will keep for a long time.); (v) 1 per cent. potassium iodide solution; (vi) 0·25 per cent. starch solution. *Method.*—The sample of serum (0·2 ml.) is accurately measured into a small centrifuge tube, treated with 0·5 ml. of the ammonium oxalate solution, allowed to stand overnight, and centrifuged (15 minutes at 3000 rev. per minute) after the addition of 1 ml. of distilled water. The precipitate is washed three times with 3 ml. of the ammonia solution, then dissolved in 0·5 ml. of the sulphuric acid on the hot water-bath, cooled, and treated with 2 ml. of the ceric solution. After 3 minutes a few drops of the potassium iodide solution and the indicator are added, and the liquid is titrated with thiosulphate solution. The results thus obtained agreed very closely with those given by determinations on the macro-scale. J. W. M.

Volumetric Micro-determination of Sugar in Blood (Plasma, etc.). F. Rappaport and R. Pistiner. (*Mikrochem.*, 1934, **15**, 111–113.)—The Hagedorn-Jensen method is used for 0·02 ml. of blood, with slightly smaller apparatus and amounts of reagents, and with a phosphate-buffered potassium ferricyanide solution, as used by Akiji and Iwatake (*Biochem. Z.*, **1932**, **242**, 43); this consists of (*a*) 0·9 g. of potassium ferricyanide dissolved in 1 l. of water, and (*b*) 21·0 g. of anhydrous potassium phosphate and 63·75 g. of tertiary potassium phosphate dissolved and diluted to 1 l. Equal parts of (*a*) and (*b*) are mixed just before use, and 2 ml. of the mixture are taken. For the titration 0·001 *N* thiosulphate solution is used in a micro-burette. J. W. M.

Colorimetric Micro-Determination of Caffeine. G. Denigès. (*Compt. rend.*, 1934, **199**, 1622–1623.)—The chloroform solution of the caffeine is evaporated to dryness at a low temperature in a porcelain casserole about 5 cm. in diameter, and the residue is treated with six drops of saturated bromine water and with a little *N* hydrochloric acid. By continuous circular movement of the vessel over the tip of a Bunsen flame, the liquid is evaporated to dryness, the residual film being similarly heated until it becomes completely orange-red (no trace of yellow). Ten ml. of water and 1 drop of 5 per cent. mercuric acetate solution (5 g. of the acetate dissolved, with heating, in 100 ml. of water containing 2 ml. of glacial acetic acid) are introduced and stirred until the residue is dissolved. The garnet-red liquid is transferred to a test-tube, 12 to 15 mm. wide, and its colour compared with those of standards similarly prepared and containing from 0·1 to 1·2 mg. of caffeine; such standards retain their colour well. If the mercuric acetate used is replaced by a zinc acetate solution of the same strength, the resultant colour is yellow and also serves for colorimetric comparison. T. H. P.

Mercurimetric Iodine Determination with Diphenylcarbazide as Indicator. J. V. Dubsky and J. Trtílek. (*Mikrochem.*, 1934, **15**, 95–99.)—Diphenylcarbazide, in 2 per cent. alcoholic solution, is used as a sensitive indicator for either micro- or macro-mercurimetric determinations of iodine. The intense violet colour formed with $Hg^{\cdot\cdot}$ is very easy to see, even in the presence of the insoluble mercury iodide formed in the titration. J. W. M.

Macro- and Micro- Tests for Nitrous Acid. J. V. Dubsky, J. Trtílek and A. Okáč. (*Mikrochem.*, 1934, **15**, 99–106.)—Chrysean ($C_4H_5N_3S_2$) can be used as a spot test reagent to identify 0·25γ of nitrite in 1 part in 2 millions dilution. A drop of the test solution is treated on the spot plate with the cold alcoholic solution of the reagent and a drop of dilute hydrochloric acid. To simplify the procedure the reagent may be used in acidified solution. Fairly concentrated nitrite solutions give a red-brown precipitate at once, whilst very dilute solutions give only a red solution, from which a precipitate slowly separates; the precipitation is accelerated by warming. The reaction is specific only in the absence of cations of the hydrogen sulphide and ammonium sulphide groups. Large amounts of nitrate give a yellow-red to red colour, but no precipitate, even on warming; in solutions of nitrates of concentrations below 2 *N* no reaction takes place. As nitrous acid is quantitatively precipitated by chrysean, and the precipitate is readily filterable, the reaction is recommended for the separation of nitrous acid from nitric acid. For this purpose an excess of a saturated solution of chrysean is used, and the precipitate filtered after the mixture has been warmed. The nitrate is identified in the filtrate by the diphenylamine reaction.

Similar diazotisation tests were also carried out with a number of other dyestuffs, but, except with safranine, an ammoniacal solution of α-naphthol was used for the coupling, instead of the coupling being effected with a further molecule of the same compound. The sensitivity of the tests is shown in the following table:

Dyestuff	Limit of identification γ	Concentration limit	Colour change
Primuline	0·3	1:100,000	Bright yellow→red
Pure yellow S	0·7	1:43,000	Yellow→blue
Safranine	1·5	1:20,000	Violet→blue
Victoria violet	15·0	1:2000	Red violet→blue

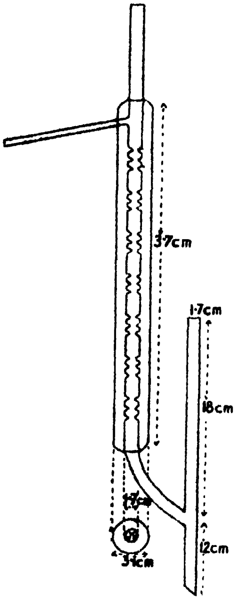
It should be noted that, whilst the limit of identification remains similar, the concentration limit varies with the depth of solution observed. J. W. M.

Collected References. Fluorescence Methods in Micro-analysis. M. Haitinger. (*Mikrochem.*, 1934–35, 16, 321–356.)—The account consists of a description of general methods and sources of light (13 references), and then more detailed description of the methods applied to inorganic analysis (40 references), organic analysis (75 references), and the examination of biological material (10 references). Among the inorganic elements and compounds detected by fluorescence methods are:—Sodium, aluminium, beryllium, zinc, zinc oxide, arsenic and antimony, bismuth, manganese and antimony, cadmium, boric acid, sulphurous acid, the rare earths, and uranyl compounds. The general types of fluorescence of various aliphatic and aromatic organic compounds are briefly described, and there is an outline of the determination of hydrogen-ion concentration in organic compounds. Fluorescence tests for the following compounds are described in detail:—β-naphthol and resorcinol, malic acid, tartaric acid, citric acid, 1.2-dicarboxylic acids, aliphatic amines, pyrrole derivatives, phthalic acid, diethyl esters, and pyridine bases. J. W. M.

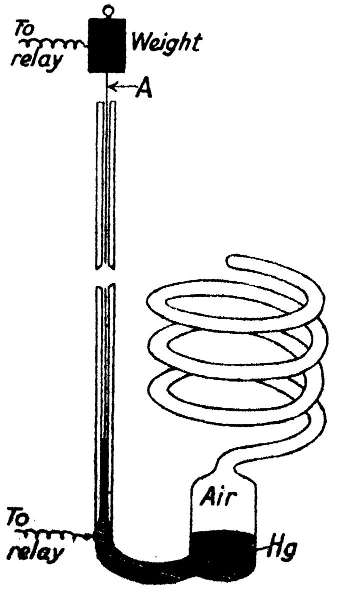
Physical Methods, Apparatus, etc.

Light Filters for the Mercury Lamp. E. J. Bowen. (*J. Chem. Soc.*, 1935, 76.)—In order to obtain a concentrated beam of light, a filter *A*, *B* or *C* is placed in a 500-ml. flask, 10 cm. in diameter (glass for the visible region and 366$m\mu$, and silica for the ultra-violet), near the lamp, followed by *D* or *E* and/or the other filters mentioned, the test solution being behind a diaphragm about 24 cm. from the lamp. *A*.—145 g. of nickel sulphate (6 to 7 H_2O) and 41·5 g. of cobalt sulphate (7 H_2O) in 1 l. of water (10 cm.). *B*.—4·4 g. of copper sulphate (5 H_2O)and 150 ml. of ammonia (sp.gr. 0·88) in 1 l. of water (10 cm.). *C*.—13 g. of copper sulphate, 0·44 g. of potassium dichromate and 50 ml. of concentrated sulphuric acid in 1 l. of water (10 cm.). *D*.—Chlorine gas at 1 atm. (3 cm.). *E*.—A saturated solution of uric acid (1 cm.). For 248 and 254$m\mu$, *A*, *D* and 0·108 g. of iodine and 0·155 g. of potassium iodide in 1 l. of water (1 cm.). For 265 and 270$m\mu$, *A*, *D* and carbon tetrachloride (2 mm.) or 4·5 per cent. mercuric chloride solution (1 cm.). For 275 and 280·5$m\mu$, *A* only. For 289·5, 292·5, 297, and 303$m\mu$, *A* and 2 per cent. oxalic acid (1 cm.) or 1·5 per cent. copper sulphate (1 cm.). For 313·5$m\mu$, *A*, 0·5 per cent. potassium hydrogen phthalate (1 cm.), and oxalic acid as above. For $334 m\mu$, *A*, *E*, phthalate and oxalic acid as above. For $366 m\mu$, *B* and Chance's black "ultra-violet" filter (2 to 3 mm.). For $405 m\mu$, *B*, a 0·75 per cent. solution of iodine in carbon tetrachloride (1 cm.), and a 1 per cent. solution of quinine hydrochloride in water (2 cm.). For $436 m\mu$, *B* and 75 per cent. sodium nitrite (1 cm.). For $546 m\mu$, *C* and Corning glass No. 512 (5 mm.). For 577 and $579 m\mu$, *C* and Corning glass No. 344 (3·4 mm.). The solutions containing iodine, carbon tetrachloride, phthalate, quinine or oxalic acid should be renewed frequently. Filter *A* (cf. *id.*, 1932, 2236 and Bäckström, *Naturwiss.*, 1933, 13, 251) must be free from iron salts; analytical reagents are suitable. J. G.

Fractional Distillation under Reduced Pressure. A. E. Bradfield. (*J. Soc. Chem. Ind.*, 1935, **54**, 6T.)—The Pyrex glass column shown was used successfully for the separation of two constituents of a viscid oil (b.p. 160° and 170° C. at 10 mm. pressure), which choked the ordinary types of column and caused the liquid to siphon over. It is based on the Widmer design, an essential feature being the alternate plain and "pushed-in" sections. In the present instance the outer jacket was evacuated to about 1 mm. pressure and sealed, the light jacketing of the exposed portion of the column and of the distillation-flask being sufficient to control the rate of reflux. J. G.



Thermo-Regulator for Heating and Cooling Baths. A. E. Bradfield. (*J. Soc. Chem. Ind.*, 1935, **54**, 6T.)—In the apparatus shown the weighted steel rod, *A*, is hung from a cord winding on (or unwinding from) a drum which is attached to the main spindle (lengthened if necessary) of a clock mechanism. The other end of *A* passes down the capillary stem of the regulator to the mercury surface and makes and breaks the relay operating the heating circuit, the former being connected with the mercury in the regulator. For most purposes air is a suitable medium for filling the regulator, and for a bath of 1 litre capacity a spiral of 6-mm. glass tubing, 8 to 10 ml. in capacity is required. The bath may thus be held at any desired temperature, or the rate of



heating or cooling may be adjusted by means of a movable weight on the pendulum of the clock; the apparatus is therefore particularly suitable for studying inflexions and arrests in cooling- and heating-curves of mixtures. J. G.

Reviews

DIE RÖNTGENSPEKTROGRAPHIE ALS UNTERSUCHUNGSMETHODE. By J. R. KATZ. Abderhalden, Handbuch der biologischen Arbeitsmethoden. Lfg. 436. Pp. 315. Berlin: Urban & Schwarzenberg. 1934. Price RM. 20.

The output of grotesquely misnamed "Handbooks" continues steadily, and the authoritative *Handbuch der biologischen Arbeitsmethoden*—indispensable to advanced students in the biological sciences—has increased in volume by a fascicule, paged, be it noted, from 3401 to 3716, dealing exclusively with X-ray spectrography.

In few branches of applied physics have there been of recent years advances more spectacular than in that which deals with the elucidation of the structure of organic fibres and the like bodies. In the present volume the methods of attack and the results obtained are discussed clearly and fully.

The author is not afraid to begin at the beginning, and his first principal section, "Die Versuchsmethodik der Röntgenspektrographie," is an excellent example of elementary but thorough exposition.

Succeeding sections deal with "Die Ergebnisse der Röntgenspektrographie in den einzelnen Gruppen der hochmolekularen Substanzen," "Polymorphie und Quellung der hochmolekularen Substanzen," "Die Röntgenspektrographie als Untersuchungs Methode (i) bei niedrigmolekularen Kolloiden, (ii) der feinstruktur von Muskeln, Nerven und anderen Organen," and "Ratschläge bei der Ausführung von kleineren röntgenspektrographischen Untersuchungen auf dem Gebiet der hochmolekularen Substanzen und der Kolloide."

The work is fully documented and well illustrated; it may be recommended unreservedly. A. FERGUSON

THE PRACTICE AND SCIENCE OF BREADMAKING. By D. W. KENT-JONES, Ph.D., F.I.C. Pp. 184. Liverpool: The Northern Publishing Co., Ltd. 1934. Price 7s. 6d.

This is essentially an elementary book written for bakery students and those engaged in the bakery trade. A book of this nature must encourage the application of scientific principles in the baking industry. The price places it within the reach of all.

"The baker must understand the character of the raw materials he is using and the nature of panary fermentation." This is an aim that might defeat the most astute student of cereal chemistry, but Dr. Kent-Jones brings our incomplete knowledge into a simple form which should be easily understood by all. Starch, gluten and the proteins, water, cellulose, fat, sugar, dextrin, the enzymes and mineral matter are all dealt with in the compass of 15 pages. Strict accuracy is sacrificed for simplicity in the statement that "In panary fermentation the yeast ferments the cane sugar present"; invertase, however, is also mentioned.

Bakers' raw materials are referred to, including wheats of world-wide origin; perhaps a little more space might have been given to flour-milling; the care taken in the cleaning of wheat and the general purity of flour are not emphasised as they should be. Bakery practice is dealt with fairly fully, and the chemical changes in dough fermentation are explained. The reason for the important "knock-back" is adequately stressed, as is also the need for control of yeast, temperature and humidity, but how many fermentation rooms can be maintained at 80–90 per cent. relative humidity? The comments on bread faults should be helpful to the student, although the baking conditions which accentuate the faults of high maltose are not detailed. No emphasis is laid on the matter of dough-mixing; correct mixing is a first essential, and numerous cases of badly made bread can be traced to insufficient mixing at the outset.

The questions of flavour and staling are discussed and admirably summed up as follows: "Generally speaking, correct fermentation and the use of cool doughs with sufficient yeast will produce bread which has good flavour and keeping qualities."

The chapter on nutritive value should help the baker to understand the importance of bread in the country's diet. In this simple presentation criticism may be unjustified, but the importance of absorbability of foodstuffs is not dealt with, and the statement: "If vitamin *A* is absent from a diet, a deficiency disease, as it is called, occurs," does not seem quite complete by itself.

An outline of bakery machinery includes several helpful hints, and the chapter on "Bakery Management and Laws Relating to the Baking Industry" will be useful to many. The final analytical chapter is elementary, but suffers from the lack of specific detail so necessary for beginners. Full details of procedure are given for determining the effective acidity of neutralising agents, but not for determining moisture and gluten. In the maltose test the previously published order of adding the sodium tungstate and the sulphuric acid is reversed.

Various repetitions detract somewhat from pleasurable reading, although these may be included for emphasis, but the type is clear and well set, and typographical errors are singularly few. From a perusal of the book the chemist should appreciate many of the interesting and unsolved problems of flour and breadmaking. The practical baker will get a new view of his art, and will realise to what extent the chemist can help him in his daily effort to produce bread of the highest quality.

C. W. HERD

CLINICAL AND PATHOLOGICAL APPLICATIONS OF SPECTRUM ANALYSIS, with Notes on Spectrography in Chemistry and Mineralogy, and Tables for Qualitative Analysis; being the Authorised Translation of Part II of "Die Chemische Emissionsspektralanalyse," by Dr. WALTHER GERLACH and Dr. WERNER GERLACH. Trans. by JOYCE HILGER TWYMAN. Illus. London: Adam Hilger, Ltd. Price 14s. 6d.

Mr. D. M. Smith, in his valuable monograph on "Metallurgical Analysis by the Spectrograph," states that "physical methods are now so largely used in chemical laboratories that the technique of spectrographic analysis should not present any formidable obstacles." The translation of Gerlach and Schweitzer's *Die Emissionsspektralanalyse*, however, records that the appearance of certain papers "resulted in an avalanche of enquiries respecting details, and—which was still more significant—in prolonged visits from colleagues attached to industrial establishments, who wished to become practically acquainted with the methods." These two quotations illustrate the undoubted truth that, although spectrum analysis is essentially simple and straightforward, it requires experience and skill. The present work is of great value, since it should appreciably shorten the time required to master the technique of spectrographic analysis.

As a general guide to methods of exciting arcs, sparks, etc., to the recognition of "Raies Ultimes" and the interpretation of spectra, the book is concise and well-ordered. It is, moreover, noteworthy for a new and extremely interesting advance in technique, namely, the systematic use of the high-frequency spark with a Tesla coil. This method of excitation permits of spectrum analysis of biological material *in the form received*—bone splinters, calculi, tissue sections, etc.—without the use of chemical reagents. In addition, the distribution of metals over the different parts of a specimen can be determined, *e.g.* the centre and periphery of a calculus.

The collaboration of Gerlach the spectroscopist and Gerlach the pathologist has resulted in a significant broadening of the field of usefulness of spectrum analysis, and it is very desirable that toxicologists and pathologists should learn of these advances.

The translation is good, and the illustrations add greatly to the value of the work.

R. A. MORTON

QUALITATIVE ANALYSE MIT HILFE VON TÜPFELREAKTIONEN. By FRITZ FEIGL. Second Edition. Pp. xi+513, 24 figures and 35 tables. Leipzig: Akademische Verlag G.M.B.H. 1935. Price: R.M. 28, bound; R.M. 26.40, stitched.

The first edition of this work has already been reviewed in THE ANALYST (1931, 56, 492). In view of the very great development of spot tests during the past three years, the increase in their number, and the widening of their application, a new edition of this, the only standard work on the subject, was much needed. The new edition has been very considerably enlarged, and now contains about 130 more pages than the old; this corresponds with even more matter, as the spacing of the letters is closer in the new edition than in the old, the type size remaining the same. This change, however, does not, in the reviewer's opinion, render the type any less legible, and enables the book to be produced in a convenient size.

The increase in matter is not so much in the theoretical section (142 pages, as compared with 122), which was already very carefully and amply written in the first edition, but in the number of tests described and the amplification of descriptions of tests in the presence of interfering ions. The neglect of precautions when interfering substances may be present is one of the greatest dangers attending the use of spot tests, and the author very rightly deals with this point with considerable thoroughness under the description of each test, it being usually assumed that the general group separations have been carried out.

The most important addition to the book is the new section on spot tests in organic qualitative analysis (135 pages). This describes very recent work, most of which has been published only during the past few months by the author and his co-workers, and also includes a considerable amount of previously unpublished work. Many of these organic spot tests are adaptations of well-known tests; some are the same as tests for inorganic ions, with organic reagents, used in the reverse direction, and some are entirely new colour tests.

All the tests are described with admirable clarity and great attention to detail. This is due to the fact that the author either has originated most of the tests himself, or has first-hand experience of them. The tabular summary of tests at the end of the book is very useful, although had a complete list of all the accessory reagents for the tests also been included, the tables would have been more useful to those equipping for the first time a laboratory for spot tests. The addition would, however, have entailed considerable expansion of the tables. The book is to be strongly recommended to all analysts. J. W. MATTHEWS

Publications Received

A HISTORY OF FOOD ADULTERATION AND ANALYSIS. By F. A. FILBY. With a Foreword by Dr. BERNARD DYER. Pp. 269. London: George Allen & Unwin, Ltd. Price 10s. net.

THREE PHILOSOPHERS (LAVOISIER, PRIESTLEY AND CAVENDISH). By W. R. AYKROYD. Pp. xii+227. London: William Heinemann, Ltd. Price 10s. 6d. net.

A GERMAN-ENGLISH DICTIONARY FOR CHEMISTS. By A. M. PATTERSON. Second Edition. Pp. 411. London: Chapman & Hall. Price 15s. net.

ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY. 1934. Vol. XIX. Pp. 836. Price 12s. 6d. (Members 7s. 6d.)

THE JOURNAL OF THE IRON AND STEEL INSTITUTE. Vol. 129, No. 1. 1934. Edited by K. HEADLAM-MORLEY.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE. REPORT OF THE ANNUAL MEETING, 1934. London: Burlington House, W.1. Price 15s.

BRITISH CHEMICALS AND THEIR MANUFACTURERS. London: Association of British Chemical Manufacturers. 1935.

INTERNATIONAL TIN RESEARCH AND DEVELOPMENT COUNCIL. FIRST GENERAL REPORT, 1934.

OFFICIAL YEAR BOOK OF THE SCIENTIFIC SOCIETIES OF GREAT BRITAIN AND IRELAND, 1934. Pp. vii+164. London: Charles Griffin & Co., Ltd. Price 8s. 6d. net.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, March 6th, the President, Mr. John Evans, being in the chair.

Certificates were read in favour of Frank Bell, Ph.D., D.Sc., F.I.C., James Talmadge Dobbins, A.M., Ph.D., Daniel Joseph O'Sullivan, M.Sc., F.I.C.

The following were elected members of the Society:—Albert Edward Andrews, A.I.C., William Lewis Davies, Ph.D., M.Sc., F.I.C., George William Ferguson, B.Sc., Ph.D., A.I.C., Oswald Hitchen, B.Tech.Sc., A.I.C., John Knaggs, B.Sc., Ph.D., A.R.C.S., D.I.C., F.I.C., Norman Ratcliffe, F.I.C.

Mr. Johan Ernst Nyrop was re-elected to membership of the Society.

The Annual General Meeting of the Society then followed, when the Hon. Treasurer presented the accounts for the past year, and the Officers and Council for the year 1935 were elected.

President.—John Evans, M.Sc., F.I.C.

Past-Presidents serving on the Council.—F. W. F. Arnaud, E. Richards Bolton, J. T. Dunn, Bernard Dyer, Edward Hinks, P. A. Ellis Richards, G. Rudd Thompson, J. Augustus Voelcker.

Vice-Presidents.—L. H. Lampitt, S. E. Melling, A. More, W. H. Roberts.

Honorary Treasurer.—E. B. Hughes.

Honorary Secretary.—G. Roche Lynch.

Other Members of Council.—A. L. Bacharach, H. E. Cox, F. G. Edmed, B. S. Evans, L. Eynon, R. C. Frederick, E. M. Hawkins, G. Hogan, Miss M. Roberts, C. J. H. Stock, J. R. Stubbs, R. W. Sutton, E. Voelcker.

In place of the usual Presidential Address, Dr. Bernard Dyer, at the invitation of the President and Council, gave an address embodying his reminiscences of the Society from its inception to the present day.

Obituary

FRANK EDWARD DAY

FRANK EDWARD DAY started his career as an assistant in the assaying laboratories of the late Mr. Riley in London. From 1902 until 1910 he worked in the laboratories of Messrs. Watney, Coombe, Reid & Co., at the Stag Brewery, London, where he added to his metallurgical experience a knowledge of other analytical methods and of bacteriology, as is shown in the series of papers of which he was part author during this time. His experience was further extended when, in 1910, he went to Limerick as head of the laboratory of the Condensed Milk Co. of Ireland. During his time there he published accounts of improvements in the Gerber process of determining milk-fat. When this firm closed down he returned to England and was for a time engaged in consulting work.

In 1927 he was appointed chemist to the Institute of Brewing Research Scheme and was engaged at Rothamsted Experimental Station in the analysis of the barleys and malts produced in an extensive investigation into the effects of soil, season and manuring on barley and malt quality. While on this work he devised a method of small-scale brewing which made it possible to continue the investigation into the study of the effects of barley, malt and hop quality on that of beer. With the centralisation of the Scheme at Birmingham University, in April, 1934, Day was moved there, and plans were made for the development of his brewing tests on an extensive scale. Unfortunately he suffered from a protracted illness at this time.

Recently he had recovered, but he died suddenly on December 30th, 1934, at the age of 51. He leaves a widow. His outstanding personal characteristic was a great cheerfulness and good fellowship, even in difficulties. He was the true analyst: a method, however routine, was always capable of improvement, and he was indefatigable in his endeavours to that end.

He obtained his London B.Sc. degree and was elected successively Associate and Fellow of the Institute of Chemistry.

L. R. BISHOP

Annual Report of Council

March, 1935

The roll of the Society stands at 733, an increase of 20 over the membership of last year.

The Council regrets to have to record the death of the following members:

Honorary member:	Viscount Devonport
Ordinary members:	Frank Edward Day
	Arthur Leonard Harry Garside
	George William Fraser Holroyd
	Daniel John O'Mahony
	George Egerton Scott-Smith
	Robert Rattray Tatlock
	William Elland Woolcott

Lord Devonport—at that time Mr. Hudson E. Kearley, M.P.—was elected an honorary member of the Society in June, 1896. The President, Dr. Stevenson, in proposing his election, dwelt upon the essential services that Mr. Kearley, as a member of the Select Committee of the House of Commons on Food Products Adulteration, had rendered to the Council of the Society in support of its views. The Report of the Select Committee later led to the amending Act of 1899. Lord Devonport, who was interested on a large scale in the wholesale grocery and provision trade, had long previously been in consultation with the Society on the question of desirable modifications of the law relating to food products; and he, together with Dr. Cameron, M.P. for Glasgow, and other Members of Parliament, took a prominent part in a special open meeting convened by the Society in March, 1893, for the purpose of discussing a tentative Bill which Dr. Cameron had recently introduced into the House of Commons, in the hope of hastening Government action in the same direction.

Day, who joined the Society in 1913, was formerly on the staff of the Institute of Brewing Research School, and last year he held an appointment at the School of Brewing in Birmingham. He had also been engaged in agricultural research on subjects related to the brewing industry at the Rothamsted Experimental Station. Garside, who was engaged in chemistry in Manchester, had been a member since 1901. Holroyd, a member for nine years, was in charge of the Chemistry Department of the Municipal Technical College, Blackburn. Although he was not often seen at our meetings, he was an active member of the North of England Section. O'Mahony, a very senior member of nearly 40 years' standing, was Public Analyst for Cork. Another old member was Scott-Smith, who joined the Society in 1899 and served on the Council some years later. He was Public Analyst for Chesterfield.

Tatlock, who at the time of his death was in his 98th year, joined the Society in 1876. He was the doyen of the analytical profession, and had served the Society in many capacities, becoming President in 1908–9. Up to the time of his death he continued to take an active interest in analytical chemistry, and until a few years back was an active partner in the well-known firm of which he was the senior. An obituary notice, written by Mr. R. T. Thomson, appears in The Analyst for March, 1935.

Woolcott had been a member for 13 years and was engaged in consulting practice in Liverpool.

During the year seven meetings of the Society have been held, and the following papers have been communicated:

"The Determination of Small Quantities of Fluorides in Water." By Guy Barr, B.A., D.Sc., and A. L. Thorogood, B.Sc.

"A Test for Ethylene Glycol and its Application in the Presence of Glycerol." By A. W. Middleton, B.Sc., A.I.C.

"The Detection of Diamines in Leather." By W. Mather, F.I.C., and W. J. Shanks.

"The Determination of Free Silica in Coal-Measure Rocks." By A. Shaw, B.Sc.

"A New Apparatus for Determining the Temperature of Crystallisation of Cocoa Butter." By S. A. Ashmore, B.Sc., A.I.C.

"The Determination of Small Quantities of Germanium in the Presence of Arsenic." By S. A. Coase, B.Sc.

"The Saturated Fatty Acids of Chrysalis Oil." By S. Ueno and H. Ikuta.

"The Determination of Lead in Biological Material, with Special Reference to Bone." By G. Roche Lynch, O.B.E., M.B., B.Sc., D.P.H., F.I.C., R. H. Slater, D.Sc., Ph.D., F.R.S.E., A.I.C., and T. G. Osler, M.B., Ch.B., M.R.C.S., L.R.C.P.

"The Determination of 'Ethyl' Vanillin." By H. C. Lockwood, B.Sc., A.I.C.

"The Detection and Identification of Metallic Particles in Manufactured Products." By H. C. Lockwood, B.Sc., A.I.C.

"Discussion on Quantitative Spectroscopy and its Analytical Applications."

Introduction. By J. J. Fox, O.B.E., D.Sc., F.I.C.

"Instruments used for Spectrum Analysis and Absorption Spectrophotometry." By F. Twyman, F.Inst.Phys., F.R.S.

"Quantitative Spectroscopy and its Analytical Applications." By S. Judd Lewis, D.Sc., Ph.D., F.I.C.

"The Use of the Spectrograph in Metallurgical Analysis." By D. M. Smith. A.R.C.S., B.Sc., D.I.C.

"The Identification of Common Edible Sea Fish (with Demonstration)." By C. H. Hattersley (Chief Inspector, Fishmongers Company).

"Fish Oils and their Vitamins." By Norman Evers, B.Sc., F.I.C.

"The Composition of Fish Pastes." By H. E. Cox, D.Sc., F.I.C.

"Note on Fish Pastes." By C. H. Manley, M.A., F.I.C.

"Some Observations on the Amounts of Amines and Free Ammonia in Fish Products." By D. H. F. Clayson, B.Sc., F.I.C., and L. H. Lampitt, D.Sc., F.I.C.

"Some Observations on Methods of Estimating the Degree of Preservation of White Fish." By G. A. Reay, Ph.D. (Torrey Research Station).

*"The Question of Tannin in Maté." By W. A. Woodard and A. N. Cowland.

"A Specification for Enamelled Hollow-ware." By J. H. Coste, F.I.C., and D. C. Garratt, B.Sc., Ph.D., F.I.C.

"Antimony Compounds extracted from Enamel-ware by Citric Acid Solutions." By R. H. Burns, B.Sc., A.I.C.

"Chemical Examination of the Seeds of *Santalum album* of Mysore." By Y. V. S. Iyer.

"The Chemical Examination of Furs in Relation to Dermatitis. Part V. The Action of Acid on Bandrowski's Base." By H. E. Cox, D.Sc., Ph.D., F.I.C., and J. U. Lewin, B.Sc., F.I.C.

"The Use of Infra-Red Rays for Distinguishing between Inks and Pigments." By C. Ainsworth Mitchell, M.A., D.Sc., F.I.C.

"Vitamin Potency and Associated Characteristics of Cod-liver Oil." By R. S. Morgan and H. Pritchard.

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* Work done under the Society's Analytical Investigation Scheme.

The North of England Section has held five meetings, at which the following papers have been read:

"The Micro-Determination of Molecular Weights of Volatile Liquid Compounds." By A. F. Colson, B.Sc., A.I.C.

"Note on the Determination of Chromium in the Presence of Iron, Aluminium and Phosphoric Acid." By J. Haslam, M.Sc., A.I.C., and W. Murray.

"The Composition and Freezing-point of Colostrum." By G. D. Elsdon, B.Sc., F.I.C.

"The Technique of the Freezing-point Test for Milk." By G. D. Elsdon, B.Sc., F.I.C., and J. R. Stubbs, M.Sc., F.I.C.

"Old Masters and Modern Forgeries." By Professor A. P. Laurie, M.A., D.Sc., F.R.S.E.

"The Composition of the Amniotic Fluid." By Arnold R. Tankard, F.I.C., D. J. T. Bagnall, F.I.C., and F. Morris, F.I.C.

"A Note on the Dictionary of Colour Standards of the British Colour Council." By Arnold R. Tankard, F.I.C.

"Mrs. Beeton, the Housewife and the Factory." By E. Hinks, B.Sc., F.I.C.

"The Effect of Grinding in the Power Mill on the Albuminoid Content of Feeding Stuffs." By F. Robertson Dodd, F.I.C., and C. Robertson Louden, B.Sc., F.I.C.

"The Examination of Ginger." By G. D. Elsdon, B.Sc., F.I.C., and Miss C. Mayne, B.Sc., A.M.C.T.

"The Hortvet Freezing-point Process for the Examination of Milk; Correction Factors and the Influence of Stirring." By J. R. Stubbs, M.Sc., F.I.C.

"Difficulties in Determining the *p*H Values of Various Liquids." By D. Burton, D.Sc., F.I.C.

"The Determination of Water in Foodstuffs." By H. M. Mason, M.Sc., F.I.C.

"The Determination of Moisture in Cereal Products by Distillation with Tetrachloroethane." By J. M. Tucker, B.Sc., F.I.C.

The November meeting of the Society was devoted to a discussion on Quantitative Spectroscopy and its Analytical Applications. At this meeting the Society was fortunate in having Messrs. Fox, Twyman, Judd Lewis, and D. M. Smith as the principal speakers, and the usefulness of the evening was enhanced by the excellent demonstration of apparatus which was shown by Messrs. Hilger, Ltd.

Later in the same month the Society took part in a joint meeting with the Food Group of the Society of Chemical Industry, when a demonstration of the principal kinds of edible fish was given by Mr. C. H. Hattersley, Chief Inspector, Fishmongers' Company, and a number of papers dealing with fish and fish products were read.

THE ANALYST for 1934 has 856 pages, which, once more, creates a record. The Publication Committee accepted 46 papers for publication, these covering a wide range of subjects and being concerned with the analysis of food and drugs (including vitamins), and of organic and inorganic compounds, gas analysis, and toxicological or forensic subjects.

Among the papers that gave rise to special discussion mention may be made of that on Free Silica in Coal-Measure Rocks, by Mr. A. Shaw, and that on The Determination of Lead in Biological Material, with Special Reference to Bone, this paper being contributed by Drs. Roche Lynch, Slater and Osler.

THE ANALYST also contained 51 Notes on subjects of analytical interest, the usual notes from legal cases, summaries of Government Reports, and a large number of abstracts from other journals.

An important event of the year was the publication, as a brochure, of the Assistant-Editor's Bibliography of Heavy Metals occurring in Food and Biological

Material, the separate sections of which had previously appeared serially in THE ANALYST. The Council has congratulated Mr. T. H. Pope on the completion of this valuable piece of work.

The Honorary Treasurer reports that the accounts for the past year show that the Society has maintained its usual satisfactory financial position, the income fully meeting the expenditure involved during the year.

HONORARY MEMBERSHIP OF THE SOCIETY.—The Council is very pleased to record that Professor G. T. Morgan, O.B.E., D.Sc., LL.D., F.R.S. (President of the Chemical Society), and Professor J. F. Thorpe, C.B.E., D.Sc., F.R.S. (President of the Institute of Chemistry), have consented to be elected Honorary Members of the Society.

MEMBERS OF 40 YEARS' STANDING.—Rule No. 7a, which exempts members of 40 years' standing from further payment of subscription, comes into force in 1935. In response to notices informing such members of this rule, the Honorary Treasurer has received letters from many of them, expressing their pleasure and appreciation of the Society's recognition of their long and uninterrupted membership.

STANDING COMMITTEE ON UNIFORMITY OF ANALYTICAL METHODS.—The Chairman has informed the Council that, although no reports have been published during the year, the work of the Sub-Committee is steadily progressing. Two further reports—one on the Determination of Lead in Food Colours, the other on the Determination of Unsaponified Fat in Soap—are already in draft, and it is hoped that these will soon appear in THE ANALYST.

As a result of a letter from the Government Chemist, the Milk-Products Sub-Committee has carried out tests on the methods that have been proposed as international ones for the determination of fat and moisture in cheese, and the findings of the Sub-Committee were forwarded to the international body concerned. The methods of Reports 1 to 3 of this Sub-Committee have been recommended for use by the Fédération Internationale de Laiterie.

The co-operation of the Standing Committee of the Society has been sought by the British Standards Institution in establishing the specification of a standard light for Lovibond tintometer readings, and investigation of this matter is proceeding.

During the year Dr. H. E. Cox has been appointed Chairman of the Unsaponified Fat in Soap Sub-Committee (*vice* Mr. L. V. Cocks, who has retired), and Mr. B. D. W. Luff, F.I.C., has joined the Sub-Committee as a nominee of the London Chamber of Commerce and of Messrs. Unilever, Ltd. Mr. F. Thomas, of Messrs. Williams Bros., Ltd., of Hounslow, has been appointed one of the Society's representatives on the Metallic Impurities in Food Colours Sub-Committee.

NORTH OF ENGLAND SECTION.—The Honorary Secretary of the Section reports that five meetings have been held during the year.

The Hortvet freezing-point results, contributed by members of the Section and others, have been collated; the full statement, which has been submitted to the Publication Committee, includes the results for about 3500 samples of milk. It is believed that this work of the Section will prove very useful to Public Analysts and to all concerned with the cryoscopy of milk.

A very successful Summer Meeting was held at Llandudno in June. Prof. A. P. Laurie gave a lecture on "Old Masters and Modern Forgeries," which was very much appreciated. A resolution of congratulation on having attained his eightieth birthday was sent to Dr. J. A. Voelcker.

The good attendance at meetings has been maintained. Ten new members have been enrolled during the year, and there has been only one resignation, that of a member who has left the district. Seventy-six subscriptions have been received, the highest number yet recorded.

The Honorary Secretary wishes to express his thanks to the Chairman (Prof. W. H. Roberts), the Committee and members of the Section for their loyal support and regular attendance during the year.

PROPOSED NEW SECTION OF THE SOCIETY.—The Council has approved in principle the formation of a Scottish Section of the Society on the lines of the North of England Section. The Council hopes that Scottish members will lend their full support to the scheme and will communicate with Dr. Tocher of Aberdeen on the subject.

ANALYTICAL INVESTIGATION SCHEME.—Two grants have been made from the fund, and in each case the work has been completed and accepted by the Publication Committee for publication in THE ANALYST. Five problems are still under investigation.

REPORTS OF THE SUB-COMMITTEES OF THE STANDING COMMITTEE ON UNIFORMITY OF ANALYTICAL METHODS.—The Council has hitherto accepted these reports; but has not taken the responsibility of recommending the methods laid down in them as standard methods of analysis. In view of the anticipated adoption of the methods in the three reports on the analysis of condensed milk as international standard methods, the Council at its November meeting passed a resolution formally adopting all the reports hitherto issued by the above-mentioned Sub-Committees and approving the methods laid down in them as standard methods of analysis.

BRITISH STANDARDS INSTITUTION.—In the last report of the Council it was noted that it was hoped to establish co-operation with the B.S.I. in the matter of standard analytical processes when these were required to be included in specifications issued by the British Standards Institution. Friendly negotiations are still proceeding, and it is hoped that such a scheme of co-operation will be formulated in the near future. The Council realises that a scheme of this type may greatly increase the work falling upon active members of the Society, but at the same time it appreciates the fact that our Society is the only one fit to represent analytical chemistry in this country, and must, therefore, take a predominant part in any work involved in preparing standard methods of analysis.

CONGRESSES.

Technical and Chemical Congress of the Agricultural Industries in Paris.—The Society was represented by Mr. T. H. Pope.

Fourteenth Congress of Industrial Chemistry in Paris.—The Society was represented by Dr. L. H. Lampitt.

Public Health Congress in London.—The President attended the Congress on behalf of the Society and contributed a paper to the discussion on "Food Standards and the Report of the Departmental Committee on the Composition and Description of Food."

The Council desires to thank these gentlemen who have kindly acted as its delegates.

DEPARTMENTAL COMMITTEE ON THE COMPOSITION AND DESCRIPTION OF FOOD.—The Council welcomes, on the whole, the report of the Departmental Committee on the Composition and Description of Food; and, in view of the fact that that report was issued in March of last year, expresses the hope that the Government will at an early date introduce legislation to give effect to the main findings of the Committee.

OTHER ACTIVITIES.—Among other activities to which reference should be made are the following:—

Further negotiations have taken place with the Food Manufacturers' Federation concerning the sale of jams.

The discussion on standards for vinegar and malt vinegar with the Malt Vinegar Brewers' Federation has been continued, and the suggested definitions agreed upon have been published in THE ANALYST (1935, p. 2).

The Scottish Milk Marketing Board Scheme was discussed with the Public Analysts' Association for Scotland.

The observations of the Council were obtained on a further Report of the Fertilisers and Feeding Stuffs Advisory Committee.

PRESIDENTIAL ADDRESS.—The Council has, with the approval of the President, suggested that the President be relieved of delivering the first of the two addresses which by custom have been given at the Annual General Meetings during his term of office. This year the Council has invited Dr. Dyer to address the meeting, and intends to ask some distinguished chemist to give a lecture at each alternate Annual General Meeting in the future.

The Council congratulates Prof. T. P. Hilditch and Dr. L. H. Lampitt on their appointment as members of the Food Investigation Board of the Department of Scientific and Industrial Research.

The Council desires, in conclusion, to record its thanks to those members who have so generously given up their time to further the interests of the Society by serving on various committees, within and without the Society, during the year.

JOHN EVANS, *President*
G. ROCHE LYNCH, *Honorary Secretary*

Dr. Dyer's Address at the Annual General Meeting

AT the outset of his address, Dr. Dyer pointed out that the occasion was particularly appropriate, since it was the Diamond Jubilee of the Society, which held its first regular meeting in February, 1875, when Dr. Redwood was President. Dr. Dyer also drew attention to the interesting fact that he and Mr. W. Charles Young, with whom he had talked over the telephone that morning, were the only survivors of that historic occasion. He explained that most of what he had to say had already appeared in "Fifty Years of the Society of Public Analysts," by himself and Dr. Mitchell, in 1932. Notwithstanding this, however, Dr. Dyer in his inimitable kindly way gave a most interesting résumé of the men and work of the Society, in all the activities of which he had been intimately concerned, since its inception. Much of the early work of the Society was concerned with food adulteration, which at that time was gross and widespread, although gradually analytical chemistry in general was brought within its scope, and in 1906 this was recognised when the title of the Society was enlarged to include Analytical Chemists other than Public Analysts.

Portraits of all of the successive Presidents were shown on the screen, as well as those of the eminent workers in the early days of the Society, and Dr. Dyer made them live again by his comments on their work and personalities. Several of the earlier Presidents were well known as Medical Officers of Health who had also been appointed Public Analysts, such as Dr. Hill of Birmingham and

Dr. Adams of Maidstone. Later distinguished occupants of the presidential chair included A. H. Allen, Otto Hehner, Sir Thomas Stevenson, Dr. Dyer himself, Dr. J. A. Voelcker, E. W. Voelcker and Alfred Chaston Chapman.

Dr. Dyer also touched on the history of the Society in connection with the Institute of Chemistry and the Government Laboratory, and laid stress upon the fact, that, in spite of a certain coolness and misunderstandings in earlier days, the most cordial relations had for many years existed between the Society and these bodies. Evidence of this cordiality was afforded by the presence of Sir Robert Robertson and Mr. R. B. Pilcher at the meeting.

A vote of thanks to Dr. Dyer for his delightful address was proposed by Dr. J. A. Voelcker and seconded by Mr. G. Rudd Thompson, who suggested that Dr. Dyer's set of slides should be deposited in the archives of the Society.

A Specification for Enamelled Hollow-ware

By J. H. COSTE, F.Inst.P., F.I.C., and D. C. GARRATT, B.Sc., Ph.D., F.I.C.

(*Read at the Meeting, December* 5, 1934)

Enamelled ironware vessels are largely used for culinary purposes, and most users are familiar with the rapid deterioration of the glazed surface of the interior, especially when these vessels are used for acid foods, such as fruits. This is obviously due to selective solution of the material of the glaze and "opacifier." The occurrence of outbreaks of antimony poisoning, traced to the preparation of lemonade in enamelware vessels, shows that some danger may attend their use. Monier-Williams[1] has done a considerable amount of work on the antimony-content of enamels used on ironware, but there is very little other precise information available, although it is well known that highly siliceous enamels are more resistant to attack than those in which base predominates.

About a year ago it was desired to prepare a specification for the properties of the glaze on enamelware for use in public institutions. It was primarily initiated as a measure to guard against risk of poisoning by the action of liquids on these enamels, but eventually it became apparent that the test had a very definite bearing on the quality of the enamel and its durability when in use. Sample vessels (pie-dishes, jugs, mugs, etc.) from British manufacturers of repute were obtained for examination, in order that precise data might be available for this purpose.

It was found that the action of boiling solutions of citric or acetic acid of equal hydrion concentration, poured into the vessel to be examined and allowed to remain in contact with the surface for a defined time, did not differ greatly, and it was therefore decided to use citric acid as a typical fruit acid. The action was measured by evaporating to dryness a known fraction of the acid solution which had stood in the vessel, igniting in a silica dish over a Bunsen burner and relating the weight of the mineral residue to the area of the interior of the vessel exposed to the action of the solvent. This area can usually be calculated by a little simple geometry.

When an enamel surface has once been attacked by acid, subsequent applications dissolve further smaller quantities of material, and it is, therefore, difficult to show the effect of varying strengths of acid on the same surface; but the fact that stronger solutions (at the low concentrations used) exerted a greater solvent action was shown by repeated applications of hot 0·5 per cent. citric acid solution on the same surface followed by hot 2·0 per cent. citric acid. Table I shows that, under similar conditions of time and temperature, two vessels of very different acid-resistance each yielded more material to the 2 per cent. solution than to the last previous 0·5 per cent. solution.

TABLE I

	Amount dissolved per sq. cm. (*a*) Mg.	(*b*) Mg.
With boiling 0·5 per cent. citric acid, cooled 24 hours	0·38	1·02
Action repeated on the same surface ,, ,, ,,	0·24	0·51
,, ,, ,, ,, ,, ,, ,, ,, ,,	0·21	0·17
With boiling 2·0 per cent. citric acid ,, ,, ,,	0·35	0·89

The effect of the length of time of contact between the enamel surface and acid is shown in Table II. Here, again, the difficulty of showing the effect on the same surface is apparent, but, after stabilisation of the rate of solution by continued application of 2 per cent. acid, a marked increase was seen in solvent action after 72 hours' cooling, compared with the preceding 24 hours' application, showing that length of time of contact governed the solubility of the enamel.

TABLE II

	Amount dissolved per sq. cm. Mg.
With boiling 2 per cent. citric acid, cooled 24 hours	0·81
Action repeated on the same surface ,, ,, ,, ...	0·65
,, ,, ,, ,, ,, ,, ,, ,, ,, ...	0·51
,, ,, ,, ,, ,, ,, ,, ,, ,, ...	0·33
,, ,, ,, ,, ,, ,, ,, 72 ,, ...	0·75

Table III shows the total enamel coating per unit area on some typical articles examined, with the corresponding amounts of surface-enamel material removed by treatment with 0·5 per cent. citric acid.

TABLE III

	Total enamel per sq. cm. Mg.	Material removed per sq. cm. Mg.	Acid-affected area
Bowl	73·5	4·40	Glaze dulled
Pie-dish	81·3	2·09	Glaze removed. Exposed surface rubbed off in powder
Bowl	70·9	0·17	Glaze apparently unaffected
Bowl	57·1	0·13	,, ,, ,,

The total amount of material removed from the enamel by acid treatment is sometimes remarkably high. An article recently examined yielded as much as

7·5 mg. per sq. cm. of surface to 0·5 per cent. citric acid solution in 24 hours, amounting to 1·328 g. in 250 ml. of liquid, and in many cases after one treatment with acid the opacifier could be rubbed off by hand.

It became obvious, after examination of many articles, all triple-coated, guaranteed acid-proof and free from antimony, that few enamels used commercially could be considered as substantially acid-proof, and that requirements in this direction must be based on limits of attack rather than on actual immunity.

On the basis of the results obtained, the following clause for acid-resistance was inserted in the specification:

> "Enamelware vessels will be considered to be sufficiently resistant to acid if, when filled as full as is convenient with a boiling 0·5 per cent. solution of citric acid in water and allowed to stand for 24 hours without being heated or artificially cooled, the amount of ash yielded on ignition of the residue obtained when a definite proportion of the solution is evaporated does not exceed 1·0 mg. per sq. cm. of surface exposed to the action of the acid, and if on repetition of the treatment with a fresh similar volume of the boiling acid solution not more than a further 0·5 mg. per sq. cm. is obtained."

In practice, the articles for examination are first washed out with distilled water, and the above test is then applied, loss of water by evaporation from the hot solution being prevented by covering the vessel with a glass plate. Before evaporation of the aliquot part in a silica dish the solution is well stirred, care being taken not to touch the sides of the vessel, as the surface in some cases becomes quite friable. If the residue from the first acid treatment is less than 0·5 mg., the second treatment is considered unnecessary.

Since the inclusion of the above clause in the specification 150 samples of enamelware have been examined in the Council laboratory, and the results of these are given in detail in Table IV.

Rejection of specimens not passing the acid-resistance test would appear justified from the fact that the last 50 samples showed a marked improvement in quality, a much smaller proportion of those submitted failing to pass the test, or yielding a high extract.

TABLE IV

Amount dissolved per sq. cm. Mg.	100 Specimens		50 Specimens	
	1st acid application	2nd acid application	1st acid application	2nd acid application
above 5	1	—	—	—
5 to 4	8	1	—	—
4 to 3	13	2	3	—
3 to 2	3	9	1	—
2 to 1·7	6	1	—	—
1·7 to 1·3	2	2	1	—
1·3 to 1·0	11	1	7	1
1·0 to 0·7	13	1	13	1
0·7 to 0·3	27	18	21	4
0·3 to 0·1	10	13	4	14
less than 0·1	6	2	—	—
not determined*	—	50	—	30

* These were either above the specification limit or below 0·5 mg. per sq. cm. for first application.

A clause in the specification required that all enamels were to be certified "free from antimony, lead, arsenic or other deleterious or poisonous ingredients," but many were found to contain antimony in appreciable quantity and were consequently rejected. Those which passed the "acid resistance" clause were submitted to a qualitative test for antimony. It was found by experiment that the following test was applicable:.

About 2·0 g. of the glaze, containing the opacifier, were chipped off and ground to a fine powder in an agate mortar. This was extracted with 1 : 1 hydrochloric acid for half an hour on a steam-bath, the extract was diluted and filtered, excess of oxalic acid was added to retain tin in solution with hydrogen sulphide, and the liquid was saturated with this gas. In the presence of antimony the usual orange precipitate was obtained and, if appreciable, the amount was then determined quantitatively. For this, the enamel was dissolved by evaporation with sulphuric, nitric and hydrofluoric acids, to eliminate silica, and boiled with hydrochloric acid. Any insoluble matter was fused with sodium peroxide and sodium carbonate, and the mass was extracted with hydrochloric acid. The antimony in the bulked solutions was precipitated as sulphide and determined by means of bromate (W. W. Scott).[2] Of the first hundred samples submitted for analysis, 13 contained antimony in considerable quantity, ranging from 0·34 to 2·80 per cent. calculated on the total enamel, and forty-one of the accepted samples contained traces of antimony insufficient to warrant rejection. Of the next fifty articles tested, only 3 contained antimony, and then only in traces—a marked improvement in standard. It is probable that many of the manufacturers were unaware of the presence of antimony in their goods, one firm having assured us that they had not used it for over a year. A sample of acid-resisting glaze for use on enamelware, received from a manufacturer whose finished articles had been rejected, was found to be free from antimony, and probably the source of the contamination in this case was the opacifier.

The antimony compounds extracted from enamelware by citric acid solutions are dealt with by Mr. R. H. Burns in the following paper.

Since this investigation was begun, another aspect of the importance of acid-resisting properties of enamel has shown itself—namely, the solution of boron compounds in appreciable quantities by the acid.

The question whether small quantities of boron are deleterious to health has given rise to considerable discussion, but the Government Departmental Committee on Preservatives in 1925 were unanimously of opinion that compounds of boron were sufficiently harmful to justify their total prohibition as preservatives, and it is admitted that boric acid adversely affects some people. The 1934 B.P. Codex indicates that boric acid is but slowly excreted, so that its effect is cumulative.

Table V shows that between one-third and two-thirds of the matter extracted by acid from the enamels examined consists of boric acid. Assuming the enamels to be used in the form of two-pint jugs containing half-pint quantities, then 0·5 per cent. citric acid would extract 0·4 to 1·7 grains of boric acid. These results have been obtained on samples of comparatively low acid-solubility, as the enamels of high acid extract were no longer available. By comparison, these would show boric acid contents of approximately 5 grains per half pint. Although these are not large doses compared with the Pharmacopoeia limits of 5 to 15 grains, they are sufficient to make desirable a reasonably high acid-resistance in enamelware.

TABLE V*

Specimen	Total enamel	Boric acid in enamel	1st acid extract	Boric acid in 1st extract	2nd acid extract	Boric acid in 2nd extract
Bowl	61·6	10·26	0·29	0·16		
Jug	92·6	13·66	1·20	0·36	0·98	0·33
Bowl			1·74	0·60	0·72	0·43
Jug			1·00	0·39		
Pie-dish			0·38	0·16		

* All results expressed in mg. per sq. cm.

An acid extract from an enamel examined quite recently showed a fluorine-content of 30 p.p.m. (calculated as sodium fluoride), equivalent to solution of 0·05 mg. from each sq. cm. of surface attacked. This amount in the extract is highly significant, having regard to the possibility of "fluorosis." Ainsworth[3] has recently shown that there is a connection between very small amounts (4·5 to 5·5 p.p.m.) of fluorine in water and "mottled teeth" in children, thus confirming the results of many other workers. Although the amounts of fluorine extracted from enamels are not being continuously ingested, their exclusion is desirable.

As increased amounts of both boric acid and fluorides weaken the resistance of enamels to acids, we have an added justification for the adoption of the acid-resistance test suggested in this paper.

SUMMARY.—(1) The enamel on enamelled ironware has been shown to be dissolved to a considerable extent by comparatively weak solutions of organic acids.

(2) Solubility of the enamel is dependent on the strength of acid and length of time of contact.

(3) A specification for "acid-resistance" has been formulated.

(4) In the manufacture of enamels it is not sufficient to avoid the use of known antimony compounds. The absence of antimony from the constituents should also be ensured.

(5) Acid extracts may contain appreciable quantities of boron and significant amounts of fluorine.

Our thanks are due to Mr. C. M. Willcox, M.A., B.Sc., A.I.C., for most of the "acid-resistance" figures.

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Antimony Compounds Extracted from Enamelware by Citric Acid Solutions

By R. H. BURNS, B.Sc., A.I.C.

(*Read at the Meeting, December* 5, 1934)

The following results were obtained in the course of experiments carried out, at the suggestion of Mr. J. H. Coste, in this laboratory, on samples of enamelware submitted for use in the Council's Institutions. It should be pointed out that this investigation was started before the publication of the official report by Monier-Williams on this subject.[1]

The general idea was to reproduce the conditions likely to arise in households where acid liquids, such as home-made lemonade, are prepared and stored in enamel vessels. The sample selected was a jug which passed the acid-resistance test,* and was therefore less likely to be attacked by food-acids than one of a lower silica-content.

Antimony may be present in an enamel in the ter-, quadri-, or quinquevalent condition.[2] The trioxide and pentoxide are both soluble in citric acid solution, whilst the tetroxide is insoluble. Thus in the extractions antimony in both the tervalent and the quinquevalent condition may occur. No attempt was made in these experiments to differentiate between these two forms, because it was felt that, although it is generally accepted that only soluble salts of tervalent antimony are toxic, there are insufficient data to show that salts of quinquevalent antimony are non-injurious.

So-called "lemonade crystals" vary greatly in composition, and may contain from 5 to 50 per cent. of tartaric acid, or citric acid, or both, whilst lemon juice contains approximately 8 per cent. of its weight of citric acid. Thus, the test solution used, which was 0·5 per cent. citric acid, was probably weaker and consequently less corrosive than that met with in common use.

The enamel of the vessel used in these experiments had an antimony-content of 0·98 per cent., and the surface area exposed to attack was 246 sq. cm.

In the first series of experiments, the results of which are shown in Table I, 400 ml. of boiling 0·5 per cent. citric acid solution were poured into the jug, and allowed to stand in the cold, for the number of hours stated. The solution was then poured off, and the antimony-content of 100 ml. was determined. This process was repeated five times. As will be seen, extract (2) was higher in antimony-content than extract (1), this presumably being due to the time taken for the initial glaze on the surface to be destroyed. After this, smaller amounts of antimony compounds were continuously extracted. During this treatment the enamel was visibly attacked to a slight extent, with consequent flaking. The antimony in extracts (3) and (4) was therefore re-determined after removal of suspended matter by centrifuging, the results being:—(3) 2·2 mg. per l., and (4) 2·0 mg. per l. As these figures are essentially the same as those obtained directly, they eliminate the chance of any antimony tetroxide present in the flakes being subsequently dissolved in the hydrochloric acid used in the determination, and thus causing the value for the total antimony extracted by the citric acid to be too high.

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* See preceding paper in this issue by J. H. Coste and D. C. Garratt.

TABLE I

Extract	Antimony extracted Mg. per litre	Grains per pint	Mg. per sq. cm.	Number of hours
1	3·3	0·029	0·0054	18
2	5·6	0·049	0·0091	18
3	2·1	0·018	0·0034	18
4	2·1	0·018	0·0034	18
5	3·2	0·028	0·0052	48

Next, the jug was washed out and scoured, and the above process was repeated, the antimony figures then obtained being given in Table II. It is obvious from the higher results obtained that cleaning exposes a new surface to the action of the acid, and thereby constitutes an added danger in the use of antimony enamelware in households.

TABLE II

Extract	Antimony extracted Mg. per litre	Grains per pint	Mg. per sq. cm.	Number of hours
1	7·2	0·063	0·0117	18
2	7·2	0·063	0·0117	18
3	3·5	0·031	0·0057	18
4	5·0	0·044	0·0081	18

Lastly, 400 ml. of boiling 0·5 per cent. citric acid solution were again poured into the jug, and successive amounts of 50 ml. were withdrawn and analysed after the time stated. The results are shown in Table III. They illustrate the great danger of storage in enamelware of this nature. The increase in the amount of antimony in the extracts may be considered remarkable when the hardness of the original enamel and the comparatively small total antimony-content of the glaze are taken into consideration.

TABLE III

Extract	Antimony extracted Mg. per litre	Grains per pint	Number of hours
1	3·6	0·032	18
2	8·6	0·075	90
3	10·0	0·088	162
4	14·6	0·128	360
5	20·0	0·175	498

By chipping off and weighing the enamel from a measured surface area, it was estimated that approximately 227 mg. of antimony were present in that portion of the glaze liable to attack by the citric acid solution. Of this amount, 6·5 mg. (2·9 per cent.) were extracted in the first series of experiments, 9·2 mg. (4·1 per cent.) in the second, and 5·8 mg. (2·6 per cent.) in the third, leaving 205·5 mg. (90·4 per cent.) of the total antimony undissolved. In comparing the results obtained in the third series of experiments, it must be remembered that the surface area subjected to attack was decreasing throughout the experiment by reason of the removal of liquid.

The method employed for the determination of the antimony in the extracts was a modification of the method given by Clarke,[3] in conjunction with the Reinsch test, and was as follows:

To an aliquot portion of the liquid an equal volume of concentrated hydrochloric acid was added, together with approximately 2 g. of oxalic acid, the solution was heated to boiling, 1 g. of sodium hypophosphite was added, and the solution boiled for ten minutes. The antimony present was then deposited on copper foil, dissolved off the latter with sodium peroxide, and finally estimated colorimetrically by the method given in that paper.

In examining the figures given under grains per pint in the tables, it is interesting to bear in mind that the emetic dose for soluble tervalent antimony compounds is given as equivalent to 0·18 to 0·36 grain of antimony, whilst the usually accepted maximum figure for arsenic in foods and drinks is 1/100th grain per pound or gallon, respectively.

In conclusion, whilst it is realised that the amount of antimony in the extracts obtained in this particular instance may not be definitely harmful, it is felt that the data given in this paper constitute a useful support to the case for the total prohibition of antimony in enamelware.

SUMMARY.—(1) Antimony compounds are extracted from "hard" enamels by the action of dilute citric acid solutions.

(2) Cleaning and scouring of enamel vessels expose a new surface to the action of the citric acid, with consequent increase in the amount of antimony extracted.

(3) Storage of citric acid solutions in enamelware is shown to be dangerous, owing to the rapid increase of the antimony-content of the stored solution.

(4) A slightly modified method is given for determining the antimony-content of such solutions.

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The Hortvet Freezing-point Process for the Examination of Milk: Correction Factors and the Influence of Stirring: II & III

By J. R. STUBBS, M.Sc., F.I.C.

(*Continued from p.* 154)

PART II

Investigation of Correction Factors

Criticism has been levelled against the Hortvet method for the determination of freezing-points on the ground that it does not indicate "true" freezing-points. This criticism is loosely expressed, and applies to every method of cryoscopy based on the principle adopted by Rüdorff and developed by Raoult and others, *viz.* supercooling the liquid under examination, and then inducing crystallisation by the addition of a small particle of the solid solvent. The "true" freezing-point of a solution, that is to say, the temperature at which that solution is in exact equilibrium with the solid solvent when the two are in contact with each other, so that the quantities of each remain constant in amount, is not directly indicated by any of the methods of the kind referred to above; what is obtained is a figure from which, by the application of certain factors, the "true" freezing-point may be calculated.

A more serious criticism is that passed by Monier-Williams[8] to the effect that the design of the Hortvet apparatus does not permit, at least readily, of the determination of the correction factors which are necessary for arriving at "true" freezing-points. This statement, and closely related ones, made to me by several observers, are well summed up by Monier-Williams (*loc. cit.*) in the words, "It is, in my experience, very difficult to get a satisfactory measurement of the supercooling correction, K, in Hortvet's apparatus." Consequently, attention is directed in this part of the paper to the study of correction factors in connection with the use of the Hortvet apparatus and technique.

When a dilute aqueous solution is cooled below its freezing-point and a particle of ice is introduced, freezing takes place, and the latent heat of formation of the ice warms up the solution to the observed freezing-point. The ice remains in the liquid and, therefore, if only pure ice separates, the original solution becomes concentrated to an extent which depends on the amount of ice formed. The observed freezing-point is, therefore, the freezing-point of a stronger solution than the one placed in the freezing-tube and, in consequence, the observed freezing-point is lower than the "true" freezing-point, that is, the freezing-point of the original solution. The supercooling correction, when applied to the observed freezing-point, corrects for the influence or "error" due to supercooling.

In the standard cryoscope of Hortvet the jacket surrounding the freezing-tube contains methylated spirit which facilitates the abstraction of heat by the cooling-bath, and this alcohol remains in place throughout the experiment. The cooling-bath is, therefore, removing heat from the freezing-tube and contents during the time that the temperature is rising after freezing commences, until the observed freezing-point is reached. The nett loss of heat thus caused has to be counterbalanced by the formation of more ice; the solution is, therefore, still further concentrated, and an additional correction, the "heat-transference" factor, must be determined before the "true" freezing-point can be obtained from the observed freezing-point.

In the Hortvet apparatus there is no means provided whereby these two effects, supercooling and heat-transference, can be separately studied. If the alcohol could be removed from the space surrounding the freezing-tube when it has served the purpose of accelerating the cooling of the liquid under examination, the abstraction of heat therefrom while the temperature is rising after freezing has commenced would be eliminated, assuming that the thermal insulation is perfect, enabling the effect of supercooling alone to be studied; and, by operating on the same liquid with and without alcohol in the jacket around the freezing-tube, the freezing-points obtained would provide data from which the heat-transference factor can be calculated; if the same amount of supercooling is used in each case the difference between the two freezing-points will be proportional to the heat-transference.

Monier-Williams, in the apparatus recently devised by him (1933), has included such an arrangement; the inner tube of the cooling-bath is provided with a tube and tap by which the alcohol can be removed with a suction pump. It is possible to modify the standard Hortvet apparatus in a similar way; a description and illustration of such an arrangement have been published. (Elsdon and Stubbs.[9])

The object of the withdrawal of alcohol being to isolate the freezing liquid from the influence of the cooling-bath, the freezing-tube should be kept central in the slightly larger tube of the cooling-bath in which it is placed. This was achieved, in the following experiments, by passing a thin rubber band round the lower part of the freezing-tube. This simple device, though admittedly not as satisfactory or convenient as the steel springs used by Raoult for the same purpose, or as the brass points employed by Monier-Williams, was yet quite effective; this was proved by placing the freezing-tube with the band in position on a hard, flat surface, when, in spite of the exertion of considerable downward pressure on the tube, the rubber band prevented contact between the tube and the surface.

(1) *The Supercooling Correction*

In order to ascertain the supercooling correction, separate portions of the same sample of milk were taken and supercooled to varying extents; the alcohol was then drawn off, the reading of the thermometer taken, and crystallisation induced, as usual, by introducing a particle of ice. The freezing-points corresponding to different amounts of supercooling were thus observed. From these data the "true" freezing-point, that is, the freezing-point for supercooling "nil" was ascertained in each case by means of a graph. The freezing-point depressions were plotted as ordinates and the corresponding degrees of supercooling as abscissae. The straight line passing through these points, produced, gives at the intersection with the axis of ordinates, the freezing-point for supercooling "nil."

It was originally intended to employ four different amounts of supercooling for each sample of milk, *viz.* about 1·5, 1·0, 0·8, and 0·5° C. It was found, however, that the differences in the readings of the thermometer corresponding to these different amounts of supercooling were in the neighbourhood of 0·002°—an amount so small that the unavoidable errors of observation might possibly approach the same order. It was, therefore, decided to employ only two different amounts of supercooling, as widely apart as practicable, say about 1·5° and 0·8°, and to increase the number of samples examined.

It was stated by Hortvet that, unless a much greater amount of supercooling than 0·5° is employed in the use of his cryoscope and technique, the rise of the mercury column is not sufficiently pronounced, and that there is more or less wavering, so that difficulty arises in deciding on the exact point at which the top of the column becomes stationary. Elsdon and Stubbs (*loc. cit.*)[9] found the same result when using a supercooling of less than about 0·8°; the mercury rose very slowly, and did not maintain a steady position for any appreciable time, and the proper freezing-point might not, under these circumstances, be attained.

In the first experiments, made with the object of ascertaining the supercooling correction, it was observed that where the amount of supercooling was small, that is, less than say 0·75°, even in the absence of alcohol in the jacket surrounding the freezing-tube, the rise of temperature, when freezing occurred, was very slow—so slow, indeed, as to suggest doubts whether the thermometer would indicate the freezing-point of the milk, influenced only by supercooling, owing to the reading being affected by the length of time which elapses and the possibility of imperfect thermal insulation, causing a nett loss of heat from the freezing tube and contents. To give an instance; in an experiment when the supercooling was 0·71° the time required for the mercury column to rise until, on observation through the telescope with the aid of the horizontal cross-wire, the ascent became imperceptible, was 9¾ minutes, as compared with about 3¼ minutes when the same milk was supercooled 1·49°. It will be seen later that, in the absence of alcohol in the space surrounding the freezing-tube, the heat insulation of the milk is not perfect; a nett loss of heat occurs, for it is possible to carry through a freezing-point determination under such conditions. The difference between the two methods of working—with and without alcohol—results in a longer time being required for the cooling of the milk when the space around the freezing-tube is occupied by air.

There were also the difficulties of judging when the rising column of mercury had reached the highest point, due to the very slow movement which occurred in that region, and of getting satisfactory readings, owing to the short time that elapsed before a fall took place.

The idea of following strictly the Hortvet technique, as regards stirring, for these particular experiments was therefore abandoned. In the first series of experiments, the results of which are recorded in Table III, four or five stirrings of three strokes each were employed, and in the second series the mechanical stirrer, working at the rate of 40 strokes per minute, was in operation all the time, the thermometer rising until tapping became necessary. It does not appear that these variations in stirring caused any significant differences in the results obtained, but the times of rising of the mercury, after two different extents, large and small, of supercooling, were diminished and rendered less unequal, and the observation of the highest point reached by the thermometer, in the case of the lesser extent of supercooling, was made more satisfactory.

One is prepared to admit that, other things being equal, it would have been preferable to carry out these experiments by following the Hortvet technique as regards stirring, but, unfortunately, it was found impossible to obtain, with small amounts of supercooling, readings considered to be satisfactory.

One observation may be recorded here, although, at present, it is not claimed that any particular significance is attached to it. When the lesser amount of supercooling was employed it was invariably found that the rise of the mercury column, after tapping the thermometer, was greater than in the case of the larger extent of supercooling. As the result of several experiments it was found that this increment was about 0·030° in the former instance, and about 0·003° in the latter.

In order to eliminate the effect of variations in the dimensions or thickness of the freezing-tubes the same tube was used for the two experiments on the same milk.

TABLE III

The Effect of Supercooling in the Hortvet Apparatus

	Degrees of supercooling	Δ	K
(*1st series*) *read by hand-lens*			
66070 M.D.	1·46	0·553	0·013
	0·74	0·548	
42127 Bn.D.	1·47	0·540	0·008
	0·78	0·537	
36219 L.D.	1·59	0·543	0·009
	0·74	0·539	
7011 D.	1·45	0·536	0·012
	0·80	0·532	
60031 A.D.	1·47	0·545	0·013
	0·88	0·541	
33566 Rs.D.	1·43	0·543	0·011
	0·76	0·539	
(*2nd series*) *read by levelled telescope*			
7039 D.	1·49	0·541	0·009
	0·62	0·537	
25441 H.B.D.	1·49	0·538	0·011
	0·78	0·534	
25446 H.B.D.	1·48	0·535	0·011
	0·81	0·531	
83704 Ws.D.	1·45	0·526	0·008
	0·75	0·523	
42267 Bn.D.	1·47	0·541	0·011
	0·78	0·537	
42268 Bn.D.	1·47	0·543	0·011
	0·80	0·539	
		Average	0·011

An equation to express the relation between the true and observed freezing-point depressions and the supercooling is given by Raoult[10] as:

$$C' = C + CSK \quad .. \quad .. \quad .. \quad .. \quad (I)$$

where C′ represents the observed freezing-point depression; C, the freezing-point depression after correction for supercooling or the "true" freezing-point depression; S, the supercooling in degrees centigrade; and K a constant.

The values for K obtained by substitution in the above equation of the ascertained values for C, C′ and S are recorded in Table III. It will be seen that the individual values vary from 0·008 to 0·013, with an average of 0·011. The greatest difference between the two extreme values for K corresponds with a difference in reading of the thermometer of rather less than 0·002°.

From the average value of K obtained above, it appears that the true freezing-point depression of a milk is increased by the fraction 0·011 of the true freezing-point depression for one degree of supercooling.

When the value of K has been determined for one particular apparatus, volume and nature of solution, and method of working, the true freezing-point may be calculated from the equation $C = \dfrac{C'}{1 + KS}$ by substituting the observed values for C′ and S, and 0·011 for K.

A rough approximation to the value of K may be calculated by a different method. It is not contended that the value so obtained is anything but approximate, but it should at least show the order of magnitude. A method similar, however, to that described below was employed by Raoult, based on the consideration of the water-values of the materials involved, and apparently regarded by him as worthy of consideration.

The formula I given by Raoult is an abbreviated form, the full expression being:

$$C = C' - \frac{CS}{L}\left(1 + \frac{r}{R}\right) \quad .. \quad .. \quad .. \quad .. \quad (II)$$

where C, C′ and S have the same significance as in the previous formula, L represents the latent heat of formation of solid solvent (for water=80); r, the water-value of the wetted parts of the freezing-tube, stirrer and thermometer (with mercury); and R, the water-value of the solution under examination.

It would appear that formula II applies only when the specific heat of the liquid in the freezing-tube is unity, and therefore R represents both the weight and the water-value of the solution. It could be made of more general application by taking into account the specific heat of the freezing liquid in cases where it differs from unity. If W is the weight in grams of a solution whose water-value is R and specific heat H, we have R = WH, and the above formula could be modified thus:

$$C = C' - \frac{CS}{L}\left(H + \frac{r}{W}\right) \quad .. \quad .. \quad .. \quad (III).$$

In the apparatus I used, where 35 ml. of milk were taken of average sp.gr. 1·03 and specific heat 0·93, the water-value of the milk = 35 × 1·03 × 0·93 = 33·5 g. The portion of the glass freezing-tube wetted by 35 ml. of milk weighed 23·5 g., and, taking the specific heat of glass as 0·197, the water-value will be 23·5 × 0·197 = 4·63 g.

The brass ring and wetted part of the stem of the stirrer weighed 4·65 g., and, the specific heat of brass being taken as 0·094, the water-value is $4{\cdot}65 \times 0{\cdot}094 = 0{\cdot}44$ g. Considering the mercury in the bulb of the thermometer as 53·4 g., estimated from the size of the bulb and neglecting the glass envelope, the water-value will be $53{\cdot}4 \times 0{\cdot}033 = 1{\cdot}76$ g. The total number of calories, therefore, required to heat up the system after one degree of supercooling will be $33{\cdot}50 + 4{\cdot}63 + 0{\cdot}44 + 1{\cdot}76 = 40{\cdot}3$. This heat is supplied by the latent heat of formation of ice at the rate of 80 calories per g. of ice. The ice formed will therefore be $40{\cdot}3 \div 80 = 0{\cdot}5$ g. in $35 \times 1{\cdot}03 = 36{\cdot}0$ g. of milk. The fraction by which the original milk is concentrated will be $0{\cdot}5/36 = K = 0{\cdot}014$.

If, owing to the small amount of stirring, the freezing-tube does not partake in the rise of temperature, the number of calories required to warm the remainder of the system to the freezing-point after one degree of supercooling will be $33{\cdot}5 + 0{\cdot}44 + 1{\cdot}76 = 35{\cdot}7$ calories. The production of this heat requires the formation of $35{\cdot}7/80 = 0{\cdot}44$ g. of ice; the resulting fractional concentration would then be $0{\cdot}44/36 = K = 0{\cdot}012$.

The expression $\frac{CS}{80}\left(H + \frac{r}{W}\right)$, contained in the formula III above when $L = 80$, represents the error in the reading of the freezing-point depression due to the concentration of the original solution resulting from supercooling. The values for H, r, L and W depending, as they do, on the instrument and on the amount and kind of liquid used—are constant for one particular apparatus and equal quantities of the same kind of solution operated on. We may therefore write K for the expression

$$\frac{1}{80}\left(H + \frac{r}{W}\right),$$

where K is a constant, and thus obtain formula I. K is the fraction of the true freezing-point depression by which, at ordinary atmospheric pressure, the true freezing-point depression is increased, if pure ice separates, for one degree of supercooling when the solution suffers neither nett loss nor gain of heat from the surroundings during freezing; it also denotes the amount of ice formed in one gram of the original solution or, if pure ice separates, the fraction by which the original liquid is concentrated, owing in each case to a supercooling of 1° C.

In the above two methods of calculating the value of K it is assumed that only pure ice separates on freezing. If there separated, in addition, one or more of the ingredients which affect the freezing-point, the reasoning would no longer be valid; the solution remaining would then be concentrated, not by an amount equal to that of the ice separated, but by a less amount depending on the quantity and nature of the ingredients, other than ice, which separated. Few observers appear to have directed their attention to the investigation of this point. Monier-Williams[11] draws the conclusion from his own work that pure ice separates from the freezing milk where only small quantities of ice, compared with the quantity of milk used, are in question.

It would appear to be a fact that very little indeed has been recorded in the literature with regard to the investigation of the freezing-point of a liquid containing several substances in solution. Raoult, H. C. Jones, Loomis and others, apparently worked generally, perhaps it could be said exclusively, with a single substance dissolved in a pure solvent.

In the equation of Raoult, quoted above, it is further assumed that the stirring is thorough, causing the ice and solution to be brought into immediate and thorough contact with each other, conditions which, if ever quite fulfilled in working with any apparatus, are certainly not fulfilled in the case of the Hortvet cryoscope and technique, or even when the Hortvet stirrer is manipulated continuously during the rise of temperature which follows the inception of freezing, as was done in the experiments recorded in Table III, second series.

It will be observed that the above average value of K is somewhat less than the approximate value calculated from the weights and specific heats of the materials constituting those portions of the apparatus which participate in the rise of temperature that takes place on freezing, and is even slightly less than the value for milk alone, *viz.* 0·93/80 = 0·0116, assuming the specific heat of milk to be 0·93. The number of investigators, however, who have determined the specific heat of milk appears to be extremely limited. Two points should be mentioned in this connection, both of which might conceivably tend to cause the value of K to be a little low. First, if the comparatively slight agitation which occurs even when the Hortvet stirrer is manipulated continuously throughout the experiment, is not sufficient to cause thorough mixing, and there is failure to warm up to the observed freezing-point the whole of the materials whose surfaces are wetted by the milk, less heat would be required, and therefore less ice would be formed, thus diminishing the value of K, as compared with the case when the whole of the system wetted by the milk is raised to the observed freezing-point. If the metal starter, by means of which a particle of ice is introduced into the liquid, is inserted when the thermometer is in position in the freezing-tube, it will be seen that the point at which crystallisation begins must always be quite near to the bulb of the thermometer, so that, whether there is stirring or not, the latent heat of formation of ice is first liberated near to the bulb of the thermometer.

Again, it has been pointed out that a longer time is required with the Hortvet technique for the mercury to assume the stationary position after only a small, as compared with a larger, amount of supercooling has been employed, and this is the case, but to a less extent, when stirring is used. Since the cooling-bath is maintained at a temperature below that of the freezing liquid, and the insulation caused by the air-jacket around the freezing-tube is not perfect, more heat will be abstracted in the case of the lesser amount of supercooling during the rise of temperature which accompanies freezing of the supercooled liquid, because the temperature then remains for a longer period in that region where the abstraction of heat is greatest in a unit of time; this will cause a slight further depression of the freezing-point in excess of that due to supercooling alone, thus bringing the reading for the lesser nearer to that for the greater supercooling, and consequently diminishing the value of K calculated from these observations.

(2) *The Heat Transference Correction*

A brief reference has already been made in this paper to the effect on the freezing-point when abstraction of heat by the cooling-bath, from the liquid in the freezing-tube, takes place while the temperature is rising from the point at which freezing is induced until the stationary position of the mercury column is reached. In the form of apparatus devised by Raoult and used in his latest work (1898), the freezing-tube containing the liquid to be examined was first cooled to about zero in a separate cooling mixture, and then placed in a slightly larger tube fitted to the cooling-bath; the freezing-tube was thus surrounded by an air-space which greatly diminished gain or loss of heat. Moreover, the cooling-bath, just before the inoculation of the liquid in the freezing-tube with ice, was adjusted to such a temperature that, at the observed freezing-point, only as much heat was extracted from the freezing-tube and contents as gained admittance from the surroundings in spite of insulation, together with that generated by stirring. This temperature of thermal equilibrium of the freezing-tube and contents with the surrounding media, called the "convergence temperature," was maintained to the end of the experiment. By so arranging the conditions of working that the convergence temperature coincided with the observed freezing-point the "error" due to heat transference was rendered negligible.

The arrangement adopted by Monier-Williams (1914) was similar in principle, but, in order to avoid the use of a separate cooling-bath, he introduced ether into the jacket surrounding the freezing-tube during the cooling process to reduce the time needed for refrigeration; this ether he removed before inducing crystallisation. In his later design of cryoscope (1933) the jacket contains 15 per cent. alcohol, which is removed, just prior to the commencement of freezing, but without any adjustment of the cooling-bath to cause the convergence temperature to coincide with the observed freezing-point.

From this, it will be seen that the Hortvet apparatus is distinguished from the other cryoscopes mentioned in that, when the technique recommended is observed, the action of the cooling-bath continues unchecked during the time the temperature is rising after freezing has begun, until the observed freezing-point is reached; if the true freezing-point is desired, a correction for the heat transference which takes place during this period must therefore be applied to the observed freezing-point, to compensate for the "error" so introduced.

The following experiments were carried out to ascertain the heat-transference factor for the Hortvet apparatus and method of working. A portion of milk was examined, the whole operation of determining its freezing-point being completed with methylated spirit in the space surrounding the freezing-tube; another observation was then made on the same portion of milk, but the alcohol was removed immediately before freezing was induced. With the second milk examined the experiment where alcohol was withdrawn was made before that in which the alcohol remained; this sequence was varied alternately in consecutive experiments.

The amount of supercooling in the experiments was, as nearly as possible, the same in every case—about 1·20°—and on only one occasion differed by as much as 0·03° C. in the two observations on the same milk. In these circumstances the supercooling correction is constant in amount for the same sample of milk, and the difference in the observed freezing-points, with and without the presence of alcohol, will be due to heat transference. The results are given in Table IV. The Hortvet technique was followed as regards stirring in all these experiments.

TABLE IV

The Effect of Heat Transference in the Hortvet Process

	With alcohol Δ	Without alcohol Δ	Difference K′C	K′
Read by hand-lens				
53425 R.D.	0·534	0·532	0·002	0·004
53426 R.D.	0·550	0·547	0·003	0·005
48051 By.D.	0·548	0·546	0·002	0·004
48052 By.D.	0·538	0·534	0·004	0·008
53428 R.D.	0·549	0·545	0·004	0·008
53430 R.D.	0·544	0·542	0·002	0·004
Read by levelled telescope				
46 Middleton	0·557	0·554	0·003	0·006
48 ,,	0·552	0·549	0·003	0·006
49 ,,	0·552	0·549	0·003	0·006
51 ,,	0·554	0·550	0·004	0·008
25447 H.B.D.	0·550	0·547	0·003	0·006
25449 H.B.D.	0·543	0·539	0·004	0·008
			Average	0·006

No difference could be observed in the freezing-point of water in experiments with or without alcohol in the outer jacket.

The correction to be applied to the observed freezing-point depression for the "error" due to heat transference has been given by Raoult as:

$$\frac{C}{L}\left(1 + \frac{r}{R}\right)\frac{z}{Z},$$

where C, L, r, and R, have the same significance as in the formula II, already given, to obtain the correction due to supercooling, and z is the time which elapses from the commencement of freezing until the temperature has become nearly stationary. Z is the time necessary for the freezing-tube and contents to cool or warm one degree by heat transference at the temperature of freezing, but without the formation of ice. This correction is positive if heat is abstracted, and negative if heat is added.

The form

$$\frac{C}{L}\left(H + \frac{r}{W}\right)\frac{z}{Z},$$

where H represents the specific heat, and W the weight of the liquid under examination, will render the formula of more general application.

Now, as, in the case of the formula given for the supercooling correction, for the same apparatus and conditions of working, and equal amounts of the same kind of solution, L, r, H and W are constant, Z is also constant under these conditions. Unless the time, z, is the same in all cases we cannot, strictly speaking replace the part of the above expression $\frac{1}{L}\left(H + \frac{r}{W}\right)\frac{z}{Z}$ by a constant. But if the time taken for the mercury to rise, when freezing takes place, is assumed to be always the same, we can *then* write

$$\frac{C}{L}\left(H + \frac{r}{W}\right)\frac{z}{Z} = CK',$$

where K′ is the fraction of the true freezing-point depression by which the true freezing-point depression is increased if pure ice separates, owing to heat transference, during the rise of temperature from the lowest to the highest point which results on freezing; it is also the amount of ice formed in one gram of the original solution during that interval, and, if pure ice separates, it represents also the fraction by which the original solution is concentrated under the same circumstances.

To obtain K′, we must first of all obtain the true freezing-point depression, C (it being assumed that no heat transference takes place) by using the formula

$$C = \frac{C''}{1 + KS} \quad \ldots\ldots\ldots \quad \text{(IV)}$$

where C″ represents the observed freezing-point depression obtained when alcohol is absent, S the degrees of supercooling, and K = 0·011. This value for C may then be substituted in formula VI, where C′ is the observed freezing-point depression with alcohol present. The values for K′ given in Table IV have been thus obtained.

These values are less than that obtained by Monier-Williams[8] for his own new apparatus, *viz.* 0·0096, which appears to indicate that there is less heat transference in Hortvet's cryoscope than in that of Monier-Williams. The difference may be due to there being less heat abstraction through the thick walls of the glass freezing-tube than through the thin sheet brass of which the tubes are composed in the E.M.B. Model of Monier-Williams' apparatus, glass being a very bad conductor of heat compared with brass, and the walls very much thicker in the former case. The stirring, too, as has been previously stated, is very much more vigorous in Monier-Williams' method of working, which will tend to promote cooling.

Attention should be directed to another point in this connection. Since the removal of alcohol, previous to the inoculation of the supercooled milk with ice, does not entirely abolish nett loss of heat from the freezing-tube and contents to the cooling-bath, the value obtained for K′ would seem to be a measure of the difference between heat transference with and without alcohol; what might be called the "residual" heat transference, that is, nett loss of heat remaining when no alcohol is used, is left undetermined and by so much the value of K′, derived from the substitution of the appropriate values in equations IV and VI, will be low.

(3) *The Total Correction in the Hortvet Process*

The total correction which should be applied to the observed freezing-point depression to obtain the true freezing-point depression, depends upon the sum of the factors due to supercooling and heat transference.

The full equation given by Raoult[10] where there is a nett loss of heat, and modified to apply to dilute solutions in general, is:

$$C' = C + \frac{CS}{L}\left(H + \frac{r}{W}\right) + \frac{C}{L}\left(H + \frac{r}{W}\right)\frac{z}{Z} \quad \ldots \quad \text{(V)}$$

which, under certain fixed conditions previously stated in this paper, may be abbreviated to:

$$C' = C + KCS + K'C \quad \ldots\ldots\ldots\ldots \quad \text{(VI)};$$

for 1 degree of supercooling this becomes:

$$C' = C + C(K + K')$$

or

$$C' - C = (K + K')C,$$

that is, the difference between the observed and true freezing-point depressions $= (K + K')C$. We have seen that $K = 0{\cdot}011$ and $K' = 0{\cdot}006$, whence

$$C' - C = 0{\cdot}017 \times C.,$$

i.e. the indicated effect of supercooling and heat transference is that the true freezing-point depression is increased by 0·017 of its value, if pure ice separates, for each degree of supercooling, and the amount of ice formed in 1 g. of the original milk is 0·017 g. when there is one degree of supercooling; also, if pure ice separates, the concentration of the original milk is increased in the same circumstances by 0·017 of its value, or approximately 1/60. The supercooling recommended by the A.O.A.C. regulations is from 1·0° to 1·2°. Taking the latter figure, the observed freezing-point depression in the Hortvet cryoscope will be $0{\cdot}011 \times 1{\cdot}2 + 0{\cdot}006 = 0{\cdot}019$ of the true freezing-point depression greater than the true freezing-point depression. If the observed freezing-point depression be taken as 0·540, then a total correction of about 0·010 is indicated as the deduction to be applied to obtain the true freezing-point depression. But it has already been pointed out that the values obtained for K and K' are probably slightly low, owing to reasons connected with the lack of thermal equilibrium of the freezing-tube and contents with their surroundings while the formation of ice is in progress and the jacket round the freezing-tube contains air only.

It should be noted that the value $KS + K'$ is not the amount which should be deducted from the observed freezing-point depression to give the true freezing-point, but the *fraction* of the true freezing-point depression, which should be so used.

PART III

SOME MISCELLANEOUS OBSERVATIONS MADE DURING THE COURSE AND ARISING OUT OF THE PRECEDING WORK

During the progress of the work that has been described in Parts I and II of this paper, many considerations arose relating more or less closely to the subjects under investigation. Some of these are mentioned in this part of the paper.

(1) *The influence of the omission of alcohol from the space surrounding the freezing-tube*

The heat transference factor in the Hortvet apparatus, although not large, might be reduced to very small dimensions if no alcohol at all were employed in the jacket surrounding the freezing-tube, and there would be also a reduction in the amount of manipulation required, as compared with that when alcohol is used, for facilitating the cooling of the milk and its removal before freezing is induced. An increase in the time required to carry out an experiment would, however, be expected.

The following observations were made:—The time which was required for 35 ml. of milk to cool from zero to −1·0°, and from −1·0° to −1·7° (*i.e.* a supercooling of approximately 0·5° and 1·2°, respectively), (*a*) with the use of methylated spirit, (*b*) without methylated spirit, the cooling-bath being maintained at −3·0° in each case, and (*c*) without spirit, with the cooling-bath kept at −7·0°. The results are given in Table V.

TABLE V

	Temperature of cooling-bath °C.	Time required to cool from		
		0·0° to −1·0°	−1·0° to −1·7°	0·0° to −1·7°
With alcohol	−3·0	2 min. 0 sec.	2 min. 0 sec.	4 min. 0 sec.
Without alcohol	−3·0	8 ,, 45 ,,	15 ,, 19 ,,	24 ,, 4 ,,
Without alcohol	−7·0	2 ,, 45 ,,	2 ,, 26 ,,	5 ,, 11 ,,

From the above table it appears that, if the use of alcohol were dispensed with, during the process of cooling, the duration of an experiment would be greatly increased, unless the cooling-bath were reduced considerably below the temperature (−3·0°) specified in the A.O.A.C. regulations. On the other hand, if the temperature of the cooling-bath be maintained at −7·0° throughout the experiment, the heat transference factor is bound to be greatly increased.

(2) *The jacket surrounding the freezing-tube*

Since there was no intention in the designing of the Hortvet apparatus to isolate the freezing-tube and contents from the action of the cooling-bath during the latter part of the experiment, no arrangement was made to have substantial clearance between them. In Raoult's later apparatus there was a clearance of about 2·5 mm., and in Monier-Williams' new design one of 2·5 to 3·0 mm. is laid down, with a lower limit of 2·5 mm. In the A.O.A.C. regulations no specification is given for the internal diameter of the metal tube of the cooling-bath—the external diameter is to be 33 mm.; the instructions also prescribe that the freezing-tube "shall fit closely" into it. The average diameter of the freezing-tubes I used was 29·8 mm., and the internal diameter of the tube containing it 32·0 mm., leaving a clearance of approximately 1 mm. only. That the heat transference was not greater than was found, was probably due to the bad thermal conductivity of glass and the nearly complete absence of stirring.

This small amount of clearance is not very easy to work with conveniently when no alcohol is used. It was therefore decided to modify the apparatus by using a wider metal tube in the cooling-bath with the ordinary type of freezing-tube, so as to give a clearance of 3 mm., and the ordinary metal tube with a narrower freezing-tube to give the same amount of clearance. It is intended to proceed with experiments along these lines.

Another difficulty in the withdrawal of alcohol from the modified standard Hortvet apparatus, is that the rubber collar at the flange of the freezing-tube is apt to make an airtight joint and so prevent the withdrawal of alcohol. This difficulty was overcome by inserting short lengths of wire between the rubber and the glass. Some more convenient arrangement is desirable should the apparatus be modified, for routine use, so as to include the withdrawal of alcohol.

Further, in connection with the thermal insulation of the freezing-tube, the following facts were observed. There is described in the preceding section an experiment in which no heat-conducting liquid was used in the jacket around the freezing-tube, and it was found that the time taken for the temperature of the milk in the freezing-tube to cool from 0 to $-1{\cdot}7°$ was about 24 minutes; in another experiment the corresponding time was 33 minutes. The experiments were carried out under exactly the same conditions except that different milks and freezing-tubes were used. It seems probable that the longer time required in the second instance was due to one or both of the following reasons:—To the external diameter of the freezing-tube being less—it could only have been slightly so—and thereby slightly increasing the insulating space, and to the thicker walls of the tube. If the effect of a slight variation in the dimensions of the freezing-tube leads to a difference of 9 minutes in the time required for cooling from 0° to $-1{\cdot}7°$, it seems an additional argument for increasing the insulating jacket to, say, about 3·0 mm., if heat transference is to be reduced to a minimum.

(3) *The measurement of the rate at which the temperature rises in the supercooled liquid after freezing commences*

In the experiments recorded in Part I of this paper, the time of rising of the mercury was taken as the period from the commencement of the rise until there was a definite retardation. The adoption of this point of pronounced retardation, to fix the end of the period of ascent, was more or less satisfactory if about equal degrees of supercooling were used in the neighbourhood of 1·2° or more; but when the supercooling was less than 0·8 or 0·9°, the case was quite different. There does not then occur the same rapid rise followed by a definite falling off in speed near the highest point; the rate of rising of the column diminishes gradually as it passes from a definite rise to the position when it appears to be practically stationary, and the point at which retardation begins is further from the position of rest.

Another method of procedure tried consisted in fixing the horizontal cross-wire of the levelled telescope on the top of the mercury column when retardation first occurred and repeating the operation as the mercury rose, noting the time when no further rise was perceptible.

With varying amounts of supercooling, owing to the different manner in which the rise of the mercury took place, it was considered impossible to obtain results by either method which could be claimed to be entirely satisfactory even when operating on the same sample of milk. There was, of course, a longer time registered, for the same milk, by the latter method of measurement, than when the first rapid and more obvious rise, only, was observed.

(4) *The use of a heat-conducting liquid between the freezing-tube and the cooling-bath*

It has been explained that, with the object of hastening the extraction of heat from the liquid under examination, observers have used a conducting medium surrounding the freezing-tube. Dekhuizen[12] used mercury for this purpose, whilst Monier-Williams in his earlier form of cryoscope used ether, and in the later (1933) form, 15 per cent. alcohol. Hortvet used methylated spirit, whilst Raoult left the space empty.

When a liquid is used, the surfaces of the tubes forming the jacket are certain to remain wet after the bulk of the liquid has been withdrawn, and it would appear possible that evaporation to a greater or less extent must take place, resulting in the absorption of a certain amount of heat.

Raoult states that his formula applies only when there is no condensation of moisture on the outside of the freezing-tube, and the same might be said, on theoretical grounds, concerning evaporation from the same surface.

Another point is that the conducting liquid at a temperature between, say, −1·7° and −3·0° is suddenly replaced by air at the temperature of the room; moreover, some air may be drawn through with the last portions of alcohol.

SUMMARY AND CONCLUSIONS

1. The effects of three different methods of stirring in the Hortvet apparatus have been investigated. No significant differences in the observed freezing-point of the same milk were found when following the Hortvet technique or operating the Hortvet stirrer continuously, or when using a flat and more efficient stirrer during the rise of the mercury from the lowest to the highest point as the milk froze.

2. The values obtained with the Hortvet cryoscope for the supercooling and heat transference factors cannot be considered to be entirely satisfactory; reasons are given which may account for this. It seems certain that similar criticism applies, more or less, to other cryoscopes in which the conditions of experiment are not arranged so that the convergence temperature is the same as the observed freezing-point. It would, indeed, apply in some measure to Raoult's elaborate instrument and technique, if the precaution were neglected to arrange that the convergence temperature coincides with the observed freezing-point, for, in his experiments the solution was cooled from 0° until a supercooling of 0·5° was obtained, with the temperature of the cooling-bath maintained at −5·0° to −6·0°, and an air-jacket round the freezing-tube. The Hortvet apparatus was not intended to serve for the determination of correction factors.

3. Three courses for the cryoscopic examination of milk appear to be open:
   (*a*) To use an apparatus of precision, in which the freezing liquid at the observed freezing-point is in thermal equilibrium with its surroundings.
   (*b*) To discard altogether any attempt to obtain the correction factors of supercooling and heat transference, and to use a standard apparatus and method of procedure in all experiments. The results will be comparable, notwithstanding the fact that the figures obtained differ a little from true freezing-points.
   (*c*) To standardise the apparatus used, by comparison with a method of precision, such as that of Raoult or Monier-Williams, using the same milk in each case.

My thanks are due to Mr. W. J. Shutt of the Department of Physical Chemistry, Liverpool University, for great assistance from discussions of the principles underlying cryoscopy, and for the benefit of constructive criticism to him and to Dr. Monier-Williams and Mr. A. N. Leather. I am indebted to my colleague, Mr. R. J. Taylor, for efficient and willing help in devising necessary modifications of apparatus.

I wish to thank Mr. G. D. Elsdon for interest and facilities to carry out the investigation.

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ERRATA IN PART I (ANALYST, March, 1935).—P. 148, 8 lines from bottom of page. *Omit* the words "from the thermometer."

P. 150, 2 lines from bottom of page. *For* "29·5 mm." *read* 26·0 mm.

A Modification of Thorpe and Holmes's Method for the Determination of the Total Proportions of Methyl, Ethyl, *Iso*-propyl and Propyl Alcohols

BY S. S. AIYAR, M.SC., PH.D., F.I.C., AND P. S. KRISHNAN, M.A., A.I.C.

INTRODUCTION AND SCOPE.—This investigation is the outcome of the definition of the term "spirit" under the Indian Customs Tariff, whereby methyl, ethyl, *n*-propyl and *iso*-propyl alcohols are assessable to spirit duty.

The Indian Customs Tariff defines spirit as follows:

> The words "spirit" and "spirits," where used in items 30, 31 and 32 of the Statutory Import Tariff, Part II, Schedule II, to the Indian Tariff Act, 1894 (VIII of 1894), are not confined to ethyl alcohol, but also cover all other alcohols the proof strength of which can be readily ascertained. This description does not apply to alcohols other than those that (*a*) are miscible with water in all proportions at ordinary temperatures, and (*b*) at a temperature of 51 degrees Fahrenheit have, in the pure state, a specific gravity relative to water of not more than 0·923 (twelve-thirteenths). These conditions are satisfied by ethyl, methyl, normal-propyl and *iso*-propyl alcohols.

It was found that the determination of alcohol in preparations containing *iso*-propyl alcohol by the Thorpe and Holmes method did not give the true spirit-strengths, as it does with preparations containing ethyl or methyl alcohol. Thus it became necessary to study the behaviour of these alcohols, which would be classed as "spirit" under the above definition, and to work out a modified procedure for the determination of the propyl alcohols.

Initial qualitative examination showed (i) that both *n*-propyl and *iso*-propyl alcohols are miscible with petroleum spirit; (ii) that both are partly "salted out" from aqueous solutions by sodium chloride; (iii) that they have only limited solubilities in saturated sodium chloride solution (at about 85° F.); and (iv) that both alcohols can be removed from petroleum spirit solution by water to a much larger extent than by saturated brine.

The last observation suggested that in these cases a modification of Thorpe and Holmes's method, consisting in washing the petroleum spirit extract a few times with small quantities of water following the first brine wash, might give more correct values. This has been experimentally confirmed.

EXPERIMENTAL.—The following four alcohols were examined:—Normal propyl alcohol (Kahlbaum), *iso*-propyl alcohol (pure, Merck), ethyl alcohol and methyl alcohol (absolute alcohols dehydrated and distilled in the laboratory).

The routine method, which is based on Thorpe and Holmes's procedure for the determination of ethyl alcohol in essences and medicinal preparations (*J. Chem. Soc.*, 1903, 83, 314), consisted in diluting a suitable volume of the sample to about 100 ml., saturating it with common salt, extracting twice with successive portions of 25 ml. of petroleum spirit, combining the petroleum spirit extracts, washing them twice (25 ml. each time) with saturated brine, and distilling the combined brine layers to obtain 100 ml. of distillate (Column A in Table I gives the results obtained by this method).

In the proposed procedure the modification consists in washing the combined petroleum spirit extracts twice with 25 ml. of water instead of brine. The results for this method are recorded under Column B in Table I.

The "plain distillation" consisted in diluting 25 ml. to 125 ml., distilling, and collecting 100 ml. of distillate. The results are given under Column C.

Thus, three distillations, A, B and C, were carried out for each kind of alcohol, or each strength thereof, with the results tabulated below.

TABLE I

Name of alcohol and strength	1 Proof strength of distillate; from spirit tables*			2 Calculated proof strength of original liquid by multiplication of data in column 1 by 4			3 Calculated vol. per cent. of alcohol; from appropriate alcohol tables (original liquid)		
	A	B	C	A	B	C	A	B	C
Methyl alcohol, absolute (Note 2)	48·8	48·5	48·0	195·2	194·0	192·0	Temperature correction not available		
Ethyl alcohol, absolute	43·8	44·1	44·1	175·2	176·4	176·4	99·52	100·68	100·68
n-Propyl alcohol, absolute	9·75	26·2	46·2	39·0	104·8	188·8	Table not available		
Iso-propyl alcohol, absolute	14·5	39·1	45·0	58·0	156·4	180·0	28·72	88·68	100·08
Iso-propyl alcohol, 20 per cent.	10·4	10·7	11·55	41·6	42·8	46·2	20·0	20·6	22·4
Ditto, 30 per cent.	12·7	15·0	15·7	50·8	60·0	62·8	24·5	30·2	30·6
Ditto, 40 per cent.	14·3	18·1	19·4	57·2	72·4	77·6	28·9	37·68	40·96
n-Propyl alcohol, 20 per cent.	8·9	10·4	10·7	35·6	41·6	42·8	Table not available		

Note (1). The specific gravities could not be determined at 60° F., owing to local conditions. They were determined at laboratory temperatures and appropriate corrections were applied.

Note (2). These apparently absurd figures are due to the fact that the relationship between specific gravity, volume strength and proof spirit is not identical for methyl alcohol and for ethyl alcohol, the divergence being the greatest in the region of 25 per cent. v/v, the strength that had been chosen for the experiments. The percentage by volume of methyl alcohol present could not be calculated, as temperature-correction tables for specific gravity were not available.

From the results it is clear that by using the routine procedure based on Thorpe and Holmes's principle, propyl alcohols are only partly recovered when their strength exceeds 20 per cent. v/v. The loss increases with increase in the strength of the original sample. It was also found that, by washing the petroleum spirit layer with distilled water, more of these alcohols could be recovered (see

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* "Spirit Tables," published by H.M. Stationery Office, under the authority of the Commissioners of His Majesty's Customs and Excise.

Column 3B of Table I). As the recovery was still not quite satisfactory, further experiments, in which the number of washings with water was increased, were made, with a view to ascertaining the minimum number of washings required to remove most, if not all, of the alcohols. These experiments were restricted to *iso*-propyl alcohol, as, in our experience, next to ethyl alcohol, *iso*-propyl alcohol is the solvent in most common use. In order to get some idea how the method would work in the presence of other interfering substances, a series of determinations on an artificial essence was made. The "essence" was prepared by dissolving 10 ml. each of alcohol-free orange and lavender oils in 350 ml. of *iso*-propyl alcohol, and making the solution up to 500 ml. with water. A blank solution was also prepared by diluting 350 ml. of the *iso*-propyl alcohol to 500 ml. with water. The actual "proof spirit" content of the essence was found by distillation of the blank solution.

In this and the following series of experiments with the "essence" a further slight modification was introduced, the spirituous liquids being shaken with petroleum spirit only once. The quantity, however, was increased to 50 ml. Again, in the preliminary experiments, petroleum spirit had been washed with 25 ml. of water each time, but in these later experiments only 10 ml. of water were used for each washing. Before the petroleum spirit extract was shaken with water, it was in every instance washed once with 10 ml. of saturated brine. One series of these experiments showed that, with five aqueous washings of 10 ml. each time, the alcohol could be recovered within 3 per cent. of theory.

To confirm this and to ascertain whether further washings effected any improvement, a similar "essence" was distilled under the conditions tabulated in Table II.

TABLE II

Experimental detail		Proof spirit obtained from the combined brine layer, brine wash, and aqueous washings Per Cent.	Proof spirit recovered from petroleum extract after the aqueous washing specified in column 1 by further washing twice with 50 ml. of water each time Per Cent.	Total of figures in columns 2 and 3 Per Cent.
10 ml. brine wash only	In addition to first wash with 10 ml. of brine	40·9	77·0	117·9
1. 1 × 10 ml. H_2O wash		69·3	47·2	116·5
2. 2 × 10 ml. H_2O wash		93·7	23·1	116·8
3. 3 × 10 ml. H_2O wash		107·1	9·9	117·0
4. 4 × 10 ml. H_2O wash		112·2	3·4	115·6
5. 5 × 10 ml. H_2O wash		115·9	2·3	118·2
6. 6 × 6 ml. H_2O wash		116·3	1·8	118·1

DISCUSSION OF RESULTS.—The experiments were conducted under routine laboratory conditions. From the results in column 2 it is clear that more than 5 washings serve no useful purpose. The spirit not recovered after 5 washes is only 2 parts in 118, which may be regarded as within the limits of experimental error and negligible.

It is also obvious that, for rapid routine work, the number of the washings should be reduced to the minimum consistent with efficiency.

It has been observed that the quality of the petroleum spirit affects the quantity of spirit recovered; this was especially noticeable in the experiments in which the petroleum spirit extracts were washed only once or twice with water.

METHOD RECOMMENDED.—We recommend the following modified procedure for the determination of total spirit-content when the presence of *iso*-propyl alcohol is suspected:—One hundred ml. of the alcoholic liquid (original sample or distillate) containing approximately 30 per cent. of proof spirit is saturated with common salt and shaken with 50 ml. of petroleum spirit (b.p. 40° to 60° C.), and allowed to separate. The brine layer is drawn off and the petroleum spirit extract is washed with 10 ml. of saturated brine, followed by five successive washings with 10 ml. of water. The brine layers and aqueous washes are combined and distilled, and 100 ml. of distillate are collected. The distillate is cooled to laboratory temperature, and its spirit-content is determined by the specific gravity method.

This work was carried out in the Laboratory of the New Custom House, Bombay, and is published with the permission of the Government of India.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

COLOUR REACTIONS FOR THE IDENTIFICATION OF HYDROGENATED FISH OILS

IN Tortelli and Jaffé's test (*Annali Chim. Appl.*, 1914, **2**, 80; Abst. ANALYST, 1915, **40**, 14) a transient pink colour, changing to bright green, is obtained with hydrogenated fish and marine animal oils. Davidsohn (*Z. angew. Chem.*, 1915, **29**, 560) found that hydrogenated vegetable oil also gives a green colour, and this is in accordance with our experience. As the transient rose colour described by Tortelli and Jaffé may sometimes escape notice, we have modified their test so as to obtain a persistent pink colour.

Three g. of the melted hydrogenated oil are dissolved in a test-tube in 6 ml. of a mixture of chloroform and glacial acetic acid (1 : 1). Bromine is added, drop by drop, from a burette until a very faint pink colour appears (best seen against white paper); as a rule, two or three drops are sufficient. The test-tube is then set aside, and within 10 minutes a very characteristic reddish-violet colour appears. With other oils and tallows the pink colour does not appear, but, after the addition of a few more drops of bromine, the colour gradually changes from green to brown.

The following is an alternative method of applying the test:—The melted fat (2·5 ml.) is dissolved in the mixture of chloroform and glacial acetic acid, the solution is treated with 1 ml. of a 10 per cent. solution (by weight) of bromine in chloroform, and the cylinder is allowed to stand. With a hydrogenated marine animal or fish oil the rose colour gradually changes, after a few minutes, to a deep purple, which remains unaltered for a long time. Pure hydrogenated vegetable oils give, under these conditions, either no colour or a green or greenish-yellow colour. With mixtures of hardened vegetable and marine animal or fish oils the characteristic purple colour is perceptible in the presence of as little as 5 per cent. of the latter.

The following results were obtained with samples of imported hydrogenated oils and some non-hydrogenated oils:

TABLE I

Hydrogenated Fish Oils

	Name of oils		Colour reaction	Conclusion
(1)	Edible hardened fish oil	Japan)	Purple	Hydrogenated fish oil
(2)	,, fish oil products	(do.)	do.	do.
(3)	Hydrogenated fish oil ,,	(do.)	do.	do.
(4)	Edible hardened oil	(do.)	do.	do.
(5)	,, oil product	(do.)	do.	do.
(6)	Technical hardened fish oil	(do.)	do.	do.
(7)	Edible hardened whale oil	(Denmark)	do.	do.

TABLE II

Hydrogenated Vegetable Oils

	Name of oils	Colour reaction	Conclusion
(1)	Medakol (United Kingdom)	Brown	Not a hydrogenated fish oil
(2)	Eraco (do.)	do.	do.
(3)	Hydrogenated vegetable oil, "Lotus" brand	No colour	do.
(4)	do. "Lily" brand	do.	do.
(5)	do. "Scale" brand	do.	do.
(6)	do. "Cross Swords" brand	do.	do.
(7)	do. "Wheel" brand	do.	do.

TABLE III

Non-hydrogenated Oils

	Name of oils	Colour reaction
(1)	Poppy-seed oil	Yellow
(2)	Sesame oil	do.
(3)	Olive oil	do.
(4)	Coconut oil	Brown
(5)	Castor oil	Yellow
(6)	Tallow	Brown
(7)	Ghee	do.

Mixtures of hydrogenated fish-oil products included in Table I, in the proportion of 5 and 10 per cent., with hydrogenated vegetable products in Table II, were also tested. A distinct purple shade was obtained with the 10 per cent. mixtures in half-an-hour, whilst with the 5 mixtures a faint purple colour appeared after an hour.

Dr. H. B. Dunnicliff, Special Chemical Adviser to the Central Board of Revenue, India, has applied this test in his laboratory at Lahore to a large number of samples of hydrogenated and non-hydrogenated oils, and has obtained results analogous to those given in the foregoing tables.

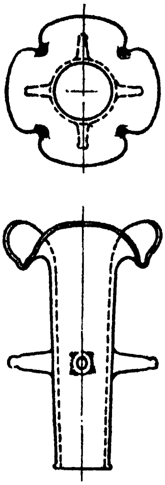
This investigation was carried out in the Chemical Laboratory, Calcutta Custom House, and the paper is published by permission of the Collector of Customs, Calcutta.

We wish to thank the Special Chemical Adviser and his assistant, Monohar Lal, for their interest in the work.

M. N. GHOSE
H. K. PAL

CHEMICAL LABORATORY
CALCUTTA CUSTOM HOUSE

ADAPTER COLLARS FOR USE IN FILTRATION



FILTRATIONS through pulp, with funnels in the necks of flasks, are apt to suffer from two evils. If the funnel fits the neck of the flask too well, it often seals it up altogether; consequently the pressure of the air inside the flask stops filtration. On the other hand, if either the funnel or the neck of the flask departs too much from the circular, the funnel is liable to be balanced precariously on two points of the neck, and a slight jar may cause the upsetting of a considerable amount of liquid from a full funnel. The collars shown in the figure were devised to remedy these two defects. Each collar consists of a piece of wide glass tubing turned over at the edge at one end to form a flange, this flange being pressed into "lips" at four points; close to the other end of the tube four small glass arms are sealed on to the wall, from which they project at right angles like the spokes of a wheel. When the tube is slipped into the neck of the flask, the glass arms should be of such a length as not to allow too much play inside the neck; the flange should be wide enough to rest on the top of the neck, the "lips" allowing free passage of air between the funnel and the neck. The funnel-stem is passed through the collar in the ordinary way; the indentations of the flange serve to hold it steady, and there is no possibility of air lock. Being made entirely of glass, the collar can easily be rinsed free of splashes.

B. S. EVANS

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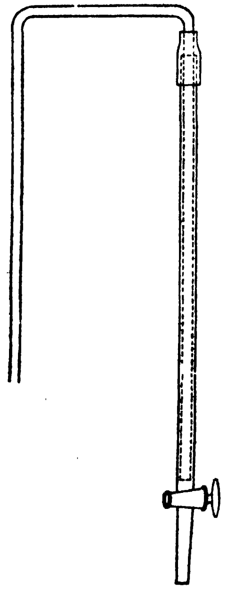

A SIMPLE SYPHONING DEVICE

THE apparatus consists of two parts: an ordinary syphon tube and a slightly wider straight tube with a tap. The width of the straight tube should be such that it will slide easily over the syphon tube; the length, from one end to the tap, a little shorter than the longer arm of the syphon. The straight tube is attached to the longer arm of the syphon by a rubber connection, fitting not too tightly, so that it can readily be slid along the arm. To use the apparatus, it is disconnected, the tap is closed, and the straight tube filled with water (or other liquid); it is then slid on to the syphon tube and pushed to the top; if the shorter arm is then immersed in the liquid to be syphoned, the straight tube drawn down to the end of the longer arm, and the tap opened, the syphon will start to flow.

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A DEVICE FOR PREVENTING THE LOSS OF STOPPERS, TAPS, ETC.

IF stoppers or taps are attached to their special vessels by means of string the latter soon rots, and is liable to break at any moment. Thin stainless iron wire is an admirable substitute for string in this respect, and will stand many months of ordinary laboratory usage before needing replacement.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FOURTH QUARTER, 1934

OF the 1290 samples of food and drugs submitted during the quarter, 100 were bought formally and 1190 informally.

TALC IN SWEETS.—A sample of cough drops contained 0·75 per cent. of talc. This was used as a dusting powder to prevent the sweets from sticking together, and it is possible that it had accumulated at the bottom of the jar in which the sweets were kept. The firm was cautioned.

"NON-BREWED TABLE VINEGAR."—This consisted of artificial vinegar. Table vinegar should be made from malt, and, as the bottle was labelled both as table vinegar and as non-brewed vinegar, there was a contradiction in terms. The firm was cautioned.

MALT VINEGAR WITH ABNORMALLY LOW CONSTITUENTS.—A sample, sold as malt vinegar, contained abnormally small percentages of solids, ash, phosphates and nitrogen, giving rise to the suspicion that vinegar other than that derived from malt was present. At an interview with one of the directors of the firm manufacturing the vinegar it was definitely stated that only malt and grain were used, and an invitation to visit the brewery and see the process was accepted. Samples of the materials used and of the product at various stages of manufacture were taken, and these are being analysed in order to try to discover the reason for the abnormally low figures.

H. H. BAGNALL

COUNTY OF KENT

REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1934

GREGORY POWDER.—One sample had been compounded in accordance with the 1914 Pharmacopoeia, whereas it should have been prepared according to the 1932 edition. The 1914 powder contained light magnesia, which in the more recent Pharmacopoeia is replaced by heavy and light magnesium carbonate.

IODINE OINTMENT.—Two samples of non-staining iodine ointment showed considerable deficiencies in iodine; they contained 0·78 and 2·0 per cent., respectively. A purchaser has every right to expect this ointment to be made according to the formulary of the British Pharmaceutical Codex, and, under those conditions, the ointment would contain approximately 5 per cent. of iodine.

POULTRY MANURE.—There has been some question as to the residual manurial value of poultry manure, the composition of which shows considerable variations. The manure may have been sold wet (green), or partly dried by the addition of earthy material or by exposure to the air. In the latter case there is usually a considerable loss of ammonia during exposure, but some poultry manure is now dried artificially by means of heat. The composition also depends to some extent upon the food of the poultry. Hence, a general price is assigned to this manure which has no real relation to the constituents of manurial value. In these circumstances compensation values for poultry manure applied might well be based on Voelcker and Hall's *Tables for Feeding Stuffs*. If the composition of the poultry manure concerned is known, there is no reason why it should be treated differently from fertilisers and the usual scale of compensation not be adopted. In the latter case the compensation award might well be one-third of the price paid, after taking one crop, and one-sixth after two crops. Though poultry manure usually acts quickly, Dr. Voelcker has shown that there is a distinct manurial value remaining after one crop.

AGRICULTURAL LIME.—Limes offered for sale vary greatly in composition, and this applies not only to those produced in the district, but also to different proprietary and well-known brands. From the analysis which makers are forced to give when selling lime it is often difficult for the farmer to assess the real value of the article offered. Burnt lime is sometimes offered in the slacked or partly slacked state, and then, in addition to the impurities originally present in the limestone, the lime will contain water, probably amounting to about 25 per cent. A carbonate of lime analysed during the quarter contained, besides other impurities, no less than 22 per cent. of sandy matter. It is, therefore, essential that a purchaser should pay great attention to the quality of lime or ground limestone which he intends to purchase, and ascertain which of the products is the cheapest.

WASTE APPLE FROM CIDER PRESSES.—This has only low manurial value, largely owing to the amount of water left in the pressings. A sample recently examined contained only 0·31 per cent. of nitrogen, 0·16 per cent. of phosphoric acid, and 0·42 per cent. of potash.

CASTOR BEAN IN GROUND-NUT CAKE.—A sample of decorticated ground-nut cake was found to contain castor bean. Although the quantity estimated in this case amounted to only 0·08 per cent., I have no doubt that it was the cause of damage to stock. The occasional occurrence of castor in feeding stuffs during the part year has caused uneasiness in the minds of many agriculturalists. In the view of some people, sufficient care is not taken by importers to ascertain that cakes are free from castor, but difficulties in this connection are due to the fact that frequently the castor bean is unevenly distributed in a feeding stuff. About a year ago I found a considerable amount of castor bean in a sample of screw-pressed linseed cake submitted to me. Although the rest of this consignment was carefully searched, there was no further evidence of castor, and the cake was fed to stock without any apparent injury. Stress has been laid upon the point that the amount of castor found in a sample of a feeding stuff is no criterion of the quantity present in the bulk, but the fact is that, when any quantity of castor is found in a part of a consignment, a far larger proportion may occur in any other part. Any prosecution for the sale of a feeding stuff containing this poisonous ingredient is rendered almost impossible on account of the difficulty of sampling on the premises on which the feeding stuff is sold or exposed or offered for sale. Although strict precautions have been taken with some foreign-pressed cake to exclude castor by the hand-picking of seed and other supervision, castor seeds still occasionally find their way into the finished cake. The appropriate Advisory Committee appointed by the Minister of Agriculture is to give consideration to the amendments of the Fertilisers and Feeding Stuffs Act, so that the declaration of the presence of poisonous materials in feeding stuffs may be made more effective.

F. W. F. ARNAUD

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

"IODINE OINTMENT": A QUESTION OF WARRANTY

ON December 10th, 1934, two summonses, issued at the instance of the Hammersmith Borough Council under the Food and Drugs (Adulteration) Act in respect of the sale of iodine ointment were heard at the West London Police Court. Evidence was given that in each case a pot labelled "iodine ointment" was purchased from a stall in Shepherd's Bush Market, and that 2d. was paid for each pot. In one case the pot was marked 1s. 3d.

The Public Analyst (Mr. F. W. Edwards, F.I.C.) reported that one of the samples contained no free iodine and no potassium iodide, and that the other contained no free iodine and only 0·4 per cent. of combined iodine. Both samples consisted mainly of coloured petroleum jelly.

The formulae of the British Pharmacopoeia, 1914, and of the British Pharmaceutical Codex, 1934, require iodine ointment to contain 4 per cent. of iodine and 4 per cent. of potassium iodide.

Both defendants pleaded guilty, and a penalty of 20s. with 21s. costs was imposed in each case.

On January 1st, 1935, a similar summons, issued by the Hammersmith Borough Council, was heard at the Kensington Petty Sessional Court.

In this case, evidence was given as to the purchase from one of the defendant's branch stores of one pot of iodine ointment. The purchase price was 3d.

The certificate of the Public Analyst showed the sample to consist of iodine 0·06 per cent.; potassium iodide, nil; combined iodine (other than potassium iodide), 0·4; and a base (mainly petroleum jelly), 99·54 per cent. The sample was therefore deficient in potassium iodide to the extent of 100 per cent. and in free iodine to the extent of 98·5 per cent.

Dr. J. B. Howell, the Medical Officer of Health for the Borough of Hammersmith, gave evidence as to the uses of iodine ointment. He said that, in his opinion, the amount of free iodine in the sample would be useless as an antiseptic, and that the use of such an ointment would confer a sense of false security upon a person using it.

For the defence it was contended that (*a*) since the current edition (1932) of the British Pharmacopoeia no longer included iodine ointment, there was now no fixed standard for the ointment; (*b*) since the Customs and Excise Authorities had agreed that the pot of ointment, with the wording as sold by the defendants, was not liable to Medicine Stamp Duty, it was not a medicine and was, therefore, outside the scope of the Food and Drugs Act; and (*c*) for commercial purposes there was a standard different from that of the British Pharmacopoeia and the British Pharmaceutical Codex. The defence further pleaded a warranty. After a lengthy hearing a fine of £15 was imposed with 5 guineas costs. It was intimated that an appeal would be lodged.

The appeal to the London Sessions was heard on March 8th. Mr. Glyn-Jones, opening the case for the respondent, described the composition of the "iodine ointment" bought from the appellants, and said that the British Pharmacopoeia 1914 and the B.P. Codex required iodine ointment to contain 4 per cent. of iodine and 4 per cent. of potassium iodide, and that the base described in the 1914 B.P. was glycerin, and prepared lard, which should be 92 per cent. No importance was attached to the difference of the base of the ointment.

The applicants had raised a defence under Section 29 of the Food and Drugs (Adulteration) Act, 1928, and relied upon a warranty from their suppliers, the manufacturers of the ointment, but the warranty was, in fact, a document which had been sent by the applicants to the manufacturers, stipulating certain conditions; and he (counsel) submitted that a warranty could not come into existence to satisfy the Act, by the act of a purchaser making a stipulation which the vendor accepted, not in writing, but by his conduct.

The Bench having discussed the case in private, Sir Percival Clarke, the Chairman, announced their decision as follows:—"The matter has been argued before us and greatly simplified by learned counsel, and it resolves itself now into practically one point, and one only, and that is whether or not the applicants have brought themselves within Sec. 29, Sub-sec. 1*b* of the Food and Drugs Adulteration Act, 1928. In that sub-section the defendant or applicant is to be discharged from the prosecution if he proves to the satisfaction of the Court, first that he purchased the article in question as the same in nature, substance and quality as that demanded of him by the person to whom he sold the article, and with a written warranty to that effect, and that he had no reason to believe, at the time he sold it that it was otherwise, and that he sold the article in the same state as when he purchased it. The main point, and practically the only point which has been argued before us, was that this was supplied with a written warranty to the effect that it was the same in nature, substance and quality as that which was supplied or demanded of him by the person to whom he sold the article. We have looked with care at the alleged warranty, and we do not think that that warranty is sufficient in itself to be described as a warranty, within the meaning of the section. As that is one of the necessary details that the applicants would have to prove, and as they have failed in satisfying us of that, the result must be that the appeal will be dismissed."

The Court allowed fifty guineas costs.

Mr. Beyfus pointed out that the applicants had bought very large quantities of goods in the belief that they had a warranty, and asked the Court to state a case upon this point of law, which might affect hundreds of other cases if they should arise.

Sir Percival Clarke agreed to do so.

"DEVONSHIRE" AND "CORNISH" CREAM IN SCONES AND CAKES

On January 18th two catering firms were summoned at the Wood Green Police Court by the Middlesex County Council for selling, respectively, cream scones and cream cakes containing fat which was not milk-fat.

Mr. R. A. Robinson, for the County Council, said that as the firms had pleaded guilty there would be no need for evidence. The facts were that at the local shops of these firms there had been sold to the public scones described by one of the defendants as "Devonshire Cream Scones," and cakes described by the other defendants as "Cornish Cream Cakes." Samples of the two articles were analysed by the Public Analyst, who reported that the cream-like substance in each case was not dairy cream, the former containing 95 per cent., and the latter 83 per cent. of fat foreign to milk-fat.

"If these articles were sold simply as cream scones and cream cakes," said Mr. Robinson, "there might be room for argument as to the propriety of their sale, but, the application of the adjective 'Devonshire' carries a certain definite and unmistakable meaning to the public mind."

The description that was given would undoubtedly be associated in the public mind with dairy cream, and it was somewhat surprising that firms of this magnitude should allow such labels to be used.

Mr. Glyn Jones, addressing the Bench on behalf of the defendants, said that it was common knowledge that the filling in cream buns bought from a baker was not, as a general rule, dairy cream at all. That fact was so well known that one could find in the dictionary the definition of the word "cream" given as follows: "Used in relation to confectionery, a cream-like substance used in the filling of cakes." The word "cream" could not be held by itself to denote "dairy cream," or otherwise the terms "boot cream" and "salad cream" would not be correct descriptions.

Since the Government made the Order forbidding the use of preservatives in cream it had been impossible to use dairy cream for confectionery purposes, unless the cakes were intended for almost immediate consumption. Bakers had, therefore, been driven to the use of substitutes. In these cases a vegetable oil of much greater purity, bacteriologically, than the ordinary standard for dairy cream had been used.

The description "Cornish" cream, counsel agreed, might lead the public to think of clotted cream, and the firm was henceforward going to omit that description.

With regard to the description "Devonshire," the word had been used by the defendant company to describe several different kinds of confectionery. The description had been applied since 1911, and he believed that the "fillings" were really Devonshire cream up to four or five years ago, when the Order as to preservatives was introduced.

In announcing the judgment of the Bench, the Chairman said that in these cases the confectionery might have looked like "Devonshire" or "Cornish," but they were described as really being such, and that was where the difference lay. Having regard to the high reputations of these firms, it had been decided to dismiss the cases under the First Offenders' Act, but to award two guineas costs in each case. It was, of course, understood that the names of these delicacies were to be revised.

Medical Research Council

REPORT FOR THE YEAR 1933–1934*

THE Report of the Committee of the Privy Council for Medical Research gives an outline of the provision made for the work of the Medical Research Council, and an account of changes in the membership of the Council and of the relations with other Government Departments.

The Report of the Medical Research Council (pp. 9–166) is divided into eight sections: I, Introduction. II, The National Institute for Medical Research. III, The Determination of Biological Standards and the Methods of Biological Assay and Measurement. IV, The Department of Clinical Research. V, External Research Schemes. VI, Industrial Health. VII, Travelling Fellowships. VIII, Conclusion.

Among the sections on subjects of chemical, as well as medical, interest are those on chemical work relating to bacteriology, and the control of the nervous system, and on the measurement of vitamins.

CHEMICAL PROBLEMS OF BACTERIOLOGY.—The researches include studies of the photodynamic inactivation of viruses, and of the conditions which allow some inactivated viruses to retain their capacity of increasing resistance to infection; the preparation of alcohol-soluble antigens from bacilli of the Salmonella group, and from the cholera vibrio. It is clear that the subject of bacteriology is being rapidly changed by the great advances in knowledge on the chemical side which are constantly being made.

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* H. M. Stationery Office. Cmd. 4796. 1935. Price 3s. net.

"*Sporogenes Accessory Factor.*"—This is a substance found by Fildes and Knight in various animal and vegetable extracts, and is favourable to the growth of many kinds of bacteria. Human urine is a good source of the principle, which has not yet been separated in a pure state, although it has been shown that it is a relatively simple, ether-soluble acid, which can be distilled in the form of an inactive methyl ester and recovered in full activity by hydrolysis.

PHARMACOLOGICAL CHEMISTRY: *Ergot.*—The search by Dr. Dudley for the water-soluble active principle of ergot has been continued, and the active substance has been separated in a sufficient degree of purity to establish its existence as a separate entity.

CARBOHYDRATE METABOLISM.—It has been found that the antiglyoxalase effect of pancreatic extract is due partly to the mono-amino acids in auto-digests of the pancreas. Further work has been done on the chemical effects of toxaemia on the activity of insulin, and on the mechanism of glycogen deposition in the liver in response to insulin on the one hand or adrenaline on the other.

STEROLS AND RELATED SUBSTANCES: VITAMIN *D*.—The new structural formula for ergosterol and the nature of the internal changes that convert it by stages into calciferol, based on the work of Adam and Askew, may be regarded as established. A critical review of recent developments in the chemistry of the sterols has been contributed by Dr. Rosenheim and Dr. King to the *Annual Review of Biochemistry.*

It has been proved that the curious absence of vitamin *D* from the brain cannot be attributed to a destructive action.

PROLONGED INHALATION OF TAR DUST, ETC.—Experiments have been continued on the continuous exposure of mice to dust from tar-treated road-surfaces, and, in addition to the high incidence of skin warts, many of which become malignant, a large increase in the occurrence and size of primary growths of the lung has been observed. No definite conclusion, however, is yet justified as to the possible relation between these results in mice and the increase in recent years of the incidence of malignant lung tumours in man.

ACCLIMATISATION OF MAMMALS TO REDUCED PROPORTIONS OF OXYGEN.—Experiments on the acclimatisation of mammals to reduced tensions of oxygen have also been continued. Reduction of the proportion of oxygen in the air to 10 per cent. cannot be tolerated indefinitely, but acclimatisation to the presence of 0·3 per cent. of carbon monoxide is more readily obtained. The effect on such acclimatisation of preliminary treatment with small doses of manganese and cobalt is under investigation.

THE MEASUREMENT OF VITAMINS.—The second International Conference on Vitamin Standardisation was held in London in June, 1934, and the standards provisionally adopted at the earlier conference, in 1931, were reviewed (*cf.* ANALYST, 1932, **57**, 521).

The standards for vitamin B_1 and vitamin D were adopted on a more permanent basis, and without immediate change. In the case of the standard for vitamin D, the Conference considered reports presented on behalf of Professor Windaus of Göttingen and Mr. Webster of the National Institute for Medical Research, which showed that the pure crystalline vitamin D (vitamin D_2, calciferol) possesses a practically unlimited stability under conditions of preservation which are easily realised. The Conference, in re-adopting the present standard, consisting of a solution in oil of a particular preparation of the mixed products obtained by irradiation of ergosterol, further decided that, if the supply should prove insufficient or the standard show signs of becoming in any respect unsatisfactory, it should be replaced by a solution in oil of the pure calciferol (vitamin D_2), the unit value of that substance being then accepted at 40,000 per milligram.

The Conference adopted pure β-carotene as the basic standard for vitamin *A* activity, in place of the provisional standard of impure, mixed carotene; the unit of measurement is the activity of a certain weight of that material. It was further decided that a subsidiary standard of cod-liver oil, the unit value of which had been accurately determined in terms of the pure carotene standard, should be prepared and held available for certain purposes.

For vitamin B_1 the standard adopted in 1931 is retained; it is a preparation made from rice polishings by the method of Jansen and Donath.

As the result of the recent work of Szent-Györgyi and others, the standard for vitamin *C* is now to be expressed in terms of *l*-ascorbic acid.

It is of interest to note that the International Conference has approved a purely physical method for the estimation of vitamin *A* in liver extracts and other rich sources; this involves the determination of the coefficient of absorption by means of a spectrophotometer, and serves as an alternative to a biological test.

INTERNATIONAL INSULIN STANDARD.—The preparation of the new international standard insulin is now approaching completion. A large quantity of the purest insulin obtainable by careful recrystallisation has been prepared by Dr. Scott on behalf of the Toronto Insulin Committee. The material is now being distributed into, and sealed in, small containers, in a perfectly dry form, and as soon as its unit value has been determined by international agreement it will be distributed in place of the relatively impure standard which has served as the world basis for insulin activity since 1925.

NATIONAL COLLECTION OF TYPE CULTURES.—The number of cultures of bacteria and micro-fungi distributed to workers at home and abroad again exceeded 5000 in the year under review, and over 200 new cultures were added to the collection at the Lister Institute. Among the new types are a *Staphylococcus aureus* strain used in the standardisation of disinfectants (Insecticide strain of Reddish), and Hungarian wine yeasts from Budapest.

Arrangements have been made with the Forest Products Research Laboratory, Princes Risborough, by which its extensive collection of wood-destroying fungi, and fungi causing discoloration in timber, will in future be listed in the publications of the National Collection. The types conserved include some 180 separate species of fungi.

Department of Scientific and Industrial Research

FOOD INVESTIGATION BOARD

REVIEW OF DEVELOPMENT DURING 1932–1933*

THE current issue of the *Index to the Literature of Food Investigation* opens with a review of 15 pages on developments during 1932 to 1933, written by Miss A. E. Glennie. The subjects are surveyed under the following headings: Gas Storage of Animal Products. Rancidity. Marine-animal Oils. Milk and Milk Products. Eggs. Freezing of Animal and Vegetable Tissues. Fruit Juices. Storage and Transport of Fruit.

The literature surveyed deals with the biochemistry, bacteriology, and chemical and physical changes of the various products, and with the problems associated with freezing, canning, and sterilisation. A reference to the abstract of the paper in this or previous volumes of the *Index* is attached to the name of each author cited.

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* *Index to the Literature of Food Investigation*, Vol. 6, No. 1 (1934). H.M. Stationery Office, 1935. Price 5s. net.

International Tin Research and Development Council

FIRST GENERAL REPORT, 1934*

THE International Tin Research and Development Council, composed of delegates appointed by the Governments of the principal tin-producing countries, has been established for the purpose of acquiring and disseminating scientific and technical knowledge relating to tin, its alloys and chemical compounds, the processes involved in the production of these materials, and their applications. The objects of the researches and other activities of the Council are to discover and develop new industrial applications of tin, to improve the existing products and processes, and to assist tin consumers in overcoming technical difficulties and problems relating to tin.

The need for an organisation for carrying out systematic research and development on behalf of the tin industry was realised by a group of tin-producing companies in 1929, and funds were provided to establish the Tin Research and Industrial Applications Committee. Several important investigations were begun and continued until the inauguration of the Council.

The present statement constitutes the first general report on the activities of the Council since its inauguration. A progress report was circulated in April, 1933, and a more comprehensive survey was submitted in October, 1933, but it was realised at the time that no adequate report could be made until a complete survey of the position with respect to tin had been undertaken in the chief industrial countries, particularly in the U.S.A.

The researches already in progress have been planned to investigate basic problems in all the major applications of tin, and the present report gives an account of the progress made in each of the chief lines of investigation.

TINPLATE.—The inspection of the tin coating on manufactured sheets of tinplate is almost entirely visual, although certain ductility tests are applied to the steel, and classification as to quality is therefore based upon obvious visible defects. Notwithstanding the knowledge gained as to the origin of these defects and methods for overcoming them, the proportion of prime plates seldom exceeds 75 per cent., and is often much less. There are also invisible defects which at present are not subjected to regular scrutiny. These consist chiefly of minute discontinuities in the coating, leaving steel uncovered by tin, with the results that rapid rusting occurs when the tinplate is exposed to moist atmospheric conditions, and that hydrogen sulphide is produced on contact with acid products, *e.g.* in the canning industry. Although methods of alleviating the trouble in some degree have been found, a real solution of the problem has not yet been discovered.

The Council's researches on tinplate, which have been carried out after discussions with tinplate manufacturers, can makers and canning research establishments, fall into the following groups:

(i) *Researches on Tinplate as Manufactured.*—Special attention has been given to the examination of tinplate manufactured under different conditions, and, in particular, with hot-rolled steel which has been normalised, to secure a fine-grained structure prior to tinning, and with the recently developed cold-rolled steel.

A new method for detecting the presence of invisible defects was developed during the research at Woolwich, and an improved process for the preliminary cleaning of the sheets prior to the test has recently been evolved. A technique for direct metallographic examination has been devised, whereby defects can be observed under the microscope at high magnification (Hoare, *J. Iron and Steel Inst.*, **1934**, **129**, [i], 253). A rapid and reliable method for determining the variation in thickness of tin coatings over the surface of the sheet has also been evolved; this is important, because the number of defects is related in some measure to the thickness of the coating.

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* Published by the International Tin Research and Development Council. 1934. Mansfield House, 378, Strand, London, W.C.2.

Much valuable information is being obtained from a study of sheets tinned under controlled conditions in an experimental tinning machine at Woolwich. This machine produces coatings on steel sheet ranging from 1 to 4 lbs. of tin per basis box, thus covering the range of commercial coatings.

It has been found possible, by a combination of hot-tinning with electrodeposition, to produce tin coatings practically free from pores.

(ii) *Defects caused by Deformation.*—The various methods of testing developed are proving of great value in investigating the causes of breaks which may appear in the coating as the result of deformation, *e.g.* in the manufacture of containers. A study has also been made of the brittle tin-iron compound which forms between the tin and the steel, and a new technique has been developed for revealing its presence and distribution (cf. *Technical Publication*, No. 2, Iron and Steel Institute).

In the course of the investigations certain distinct advantages have been established for the use of the cold-rolled tinned steel.

(iii) *Corrosion of Tinplate.*—Investigation in this field of research is being co-ordinated in Great Britain, France, Germany, Norway, and the U.S.A. In view of the differences of opinion regarding the mechanisms of corrosion, it was arranged that an analysis should be made of all the conclusions based on fact and of the hypotheses advanced to explain the facts. The survey emphasises the importance of the variation in the electric potential difference occurring between tin and steel in contact with the fluids in foodstuffs. At discontinuities in the tin coating there are set up electric currents passing between the tin and the areas of exposed steel, and corrosion of one or both metals may occur, depending on a number of conditions, such as the acidity of the foodstuff, the presence of air, etc. (cf. *Technical Publication*, No. 5, "The Electrochemical Behaviour of the Tin-Iron Couple in Dilute Acid Media," Faraday Society).

Various attempts have been made to diminish the attack on the tinplate by adding a suitable corrosion inhibitor, but, so far, the results have been uncertain and inadequate.

The work so far done on the merits of different kinds of steel tends to prove that the purer form of steel that can be used in the new cold-rolling process results not only in fewer breaks in the tin coating on deformation, but also in a lower rate of attack on the exposed steel. The cold-rolling method permits of the use of steel of higher purity, especially as regards phosphorus-content; the thickness of the steel is controlled more uniformly, and the structure is finer and more uniform than in that normally produced by hot-rolling.

SOLDERS.—Numerous technical inquiries as to the resistance of solders to corrosion have been received, and in several cases, particularly in connection with food products, it has been possible to show that the use of high-tin solders offers definite advantages. For rapid soldering operations, *e.g.* in can-making, the solder has to penetrate small crevices, and fluidity is likely to be the decisive factor in the soundness of the joint. Certain impurities, particularly liable to be introduced when secondary tin is used in the manufacture of the solder, may have a direct bearing on certain anomalies in behaviour that have been observed. Researches on this question are in progress.

WATER PIPES.—The lead alloy containing 1·5 per cent. of tin and 0·25 per cent. of cadmium has found increasing application in certain districts for water pipes, owing to the advantages of light weight and improved resistance to attack by soft water. A recent competitor is lead containing a small amount—about 0·05–0·06 per cent.—of tellurium (*cf.* ANALYST, 1933, **58**, 366).

An important direction in which tin may find an increased use in water pipes arises from the fact that certain waters have a solvent action on lead and on all the lead alloys proposed for pipes. There are grounds, therefore, for anticipating that a tin-lined pipe, whether of lead or one of the above-mentioned alloys, would be so superior as to justify the increase in cost that would be involved.

Although tin-lined lead pipes are at present being manufactured, it is considered that in their present form they are unsuitable to meet adequately the competition of pipes of other materials and that a lighter pipe is required, such as may be obtained by the use of a relatively strong lead alloy lined with tin or a tin alloy. Researches are necessary to evolve a pipe having the requisite properties, *e.g.* to withstand high water pressures, and to ensure that they will also be suitable for hot water. Data are being obtained for the Council as to the minimum thickness of tin that will ensure adequate protection of the underlying lead alloy, and also as to suitable methods of jointing, whereby no lead is exposed when two lengths of pipe are united.

ACTION OF ABRASIVES AND CLEANERS ON TIN COATING.—When the conditions for the production of satisfactory tin coatings have been clearly defined, there is still the problem of obtaining harder coatings capable of resisting the wear and cleaning operations to which they are exposed in service.

The alkaline cleaners commonly used in the dairy and other industries have a marked corrosive action on tin coatings. A study, therefore, of additions which inhibit this corrosive action without detracting from the detergent power of the cleaner, has been made. Cleaners of this type have already been introduced, but leave room for improvement. An inhibitor of considerable promise has been discovered, and, when the work has reached a suitable stage, the information will be disseminated in order to encourage the use of non-corrosive cleaners. The ease with which tin is abraded is leading to a decrease in the use of triple and quadruple tin coatings. It is anticipated that when the work on harder tin coatings is further advanced, it will be possible to recommend the use of such coatings to eliminate the troubles encountered.

Corrosive attack on tin coating is experienced in certain important applications in the brewing industry. Even small amounts of tin dissolved in this way cause the beer to become turbid. Investigations are being carried out on (1) the influence of additions of other metals to tin, and (ii) suitable treatment of the tinned surface with the object of forming a resistant film. Encouraging results have already been obtained in both these directions, and in some of the coatings now under examination the attack has been reduced to a negligible quantity. Other cases of the corrosion of tin will be investigated in the light of this investigation.

OTHER INVESTIGATIONS.—Other subjects under investigation include problems connected with bearing metals, with the preparation of alloys from powdered metals, with other lead-tin alloys, bronzes, the addition of other elements to tin, electrodeposition of tin and tin alloys, anodic oxidation and dyeing of tin, spraying of tin, collapsible tubes, tin foil, block tin pipe, tin in steel and nickel alloys, and tin compounds. A new use for tin has been found as an electrode in an accumulator; the essential features of the cell are electrodes of tin and lead peroxide, respectively, in an electrolyte of dilute sulphuric acid. The whole cell is filled with porous acid-resisting ceramic material in which the acid is absorbed, so that it is in effect a dry cell. Since no gas is evolved during use, the cell may be sealed after charging, thus preventing leakage of acid.

An investigation of the anti-knock qualities of a range of organic compounds of tin is in progress in collaboration with the research organisation of a group in the oil industry. The effects of tin compounds in diminishing the rate of oxidation of lubricating oils is also being considered.

The Report, which occupies 37 pages, concludes with an account of the Council's Bureau of Technical Information, its Statistical Office, and its facilities for technical inquiries. Arrangements have been made for technical publications of the Council to appear in three series: A, reprints of original research papers relating to the work of the Council's investigators; B, monographs setting forth existing knowledge on the various aspects of tin and its applications; C, brochures dealing with new applications of tin. A list of the publications issued up to the present is appended.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection of Altered Eggs. J. Grossfeld and J. Peter. (*Z. Unters. Lebensm.*, 1935, **69**, 16–29.)—The form of decomposition here considered is that beginning in the yolk of the egg and caused by bacteria, among which probably *Mesentericus* species predominate. As lower fatty acids (butyric, etc.) are formed, the name "cheesy" putrefaction is suggested for this change, although the expression "faecal" putrefaction is sometimes used. The extent of the alteration may be indicated by the "decomposition quotient," which represents one hundred times the ratio of the P_2O_5 soluble in isopropyl alcohol to that soluble in aqueous (95 per cent.) ethyl alcohol (*cf.* Grossfeld and Walter, *ibid.*, 1934, **68**, 270). This quotient is influenced mainly by the glycerophosphoric acid liberated by decomposition of the lecithin; in undecomposed eggs its value is theoretically 0, and when there has been complete decomposition of the lecithin it is 100. With fresh, and with old but unaltered hens' and ducks' eggs, with hard-boiled eggs, and with one water-glass egg, values of the quotient below 6 were found, both on the yolk alone and on the whole egg-content; the age of the egg does not affect the value. When cheesy putrefaction sets in, the quotient rapidly reaches high values, and the change occurring in one day at summer temperature may be considerable. Following the formation of glycerophosphoric acid, this undergoes slow breakdown, with production of phosphoric acid.

When tested similarly, fresh milk gives quotients of 71 to 80, wheaten flour 34·7 to 40, rye meal 37·4, oat flakes 29·5, and soya-bean meal 9. Egg food-pastes show values varying widely according as fresh or spoiled eggs are used in their preparation. With flours and egg food-pastes, extraction with absolute alcohol and benzene together gives practically the same results as boiling with isopropyl alcohol under a reflux condenser, and extraction with 90 per cent. alcohol the same as boiling with aqueous alcohol in a reflux apparatus. T. H. P.

New Form of Adulteration of Eggs? V. Froboese. (*Z. Unters. Lebensm.*, 1935, **69**, 14–15.)—Reference is made to a communication from a State school of poultry-breeding entitled "The Egg-yolk Colour Problem Solved," and recently published in a German poultry journal. The "solution" consists in mixing with the hens' food a cod-liver oil emulsion coloured blood-red by means of a dyestuff. This dyestuff is transported rapidly, as such, to the yolk of the eggs produced. It is claimed that this procedure does not constitute adulteration, as artificial coloration of other foodstuffs such as butter, jam, etc., is permissible.

T. H. P.

Supposed Diminution of Lecithin in Egg-Paste Products. W. Diemair, F. Mayr and K. Täufel (*Z. Unters. Lebensm.*, 1935, **69**, 1–9.)—The so-called retrogression of lecithin occurring during storage of egg food-paste products is attributable mainly to chemico-colloidal alterations in the mixture of flour and lecithin. All the observations seem to be explicable by the formation of absorption compounds of the ingredients, this resulting in depression of the solubility of the lecithin in its ordinary solvents. Any biological decomposition of the lecithin is of minor importance. Experimental results described indicate that both carbohydrates and proteins participate in the changes concerned, and that fat plays no part. In investigations on this phenomenon, treatment of the material with water prior to extraction with alcohol is inadvisable, since the amount of alcohol-soluble phosphorus is a function of the amount of water added.

T. H. P.

Distinction between Egg-yolk and Vegetable Lecithin in Food-pastes. H. Kluge. (*Z. Unters. Lebensm.*, 1935, **69**, 9–13.)—The fact that the ratio of lecithin phosphoric acid to sterols is very much greater in egg-yolk than in vegetable lecithin preparations may be utilised, in conjunction with other tests, for the detection of vegetable lecithin in food-pastes. If the egg-content of the material, as calculated from the lecithin phosphoric acid, is greater than that calculated from the sterols present, the presence of a vegetable lecithin preparation is indicated. Weyl's lutein test is also useful in this connection: the dry residue from the acetone extract is dissolved in ether and treated with solid sodium nitrite and dilute sulphuric acid. With the oil from egg food-pastes the deep yellow ethereal solution then undergoes almost complete decolorisation, whilst with that from vegetable lecithin the yellow colour persists virtually unchanged. The iodine (Hübl) value of the oil likewise furnishes useful indications; the oil from a sample of egg food-paste gave the value 70·7, whilst the oils from two products prepared with a vegetable lecithin preparation had the iodine values 117·8 and 108, respectively. An iodimetric method of determining sterols, based on Szent-Györgyi's and Tillmans' work, is described in detail. T. H. P.

Determination of Copper in Milk. L. W. Conn, A. H. Johnson, H. A. Trebler and V. Karpenko. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 15–23.)—A large number of methods have been tried. A method involving separation of the copper as sulphide or by micro-electrolysis followed by colorimetric determination with ethyl dithiocarbamate was found satisfactory. *Ashing.*—A 25- to 200-ml. sample of the milk (according to the copper-content) is evaporated to dryness in a platinum vessel, or in a quartz vessel which has previously been extracted with sodium acetate solution (according to Elvehjem, Hart and Steenbock, *J. Biol. Chem.*, 1929, **83**, 27); the copper contamination from porcelain crucibles may be considerable. The addition of 5 drops of glacial acetic acid prevents foaming.

The residue is finally ashed in a muffle-furnace at a dull red heat (not over 565° C.). *Hydrogen sulphide precipitation.*—The ash is dissolved, as far as possible, in 2 ml. or more of 20 per cent. hydrochloric acid by warming; the solution is transferred to a 15-ml. centrifuge tube and centrifuged to remove any residue. Ammonia is added until a slight permanent precipitate of calcium phosphate is formed, and the solution is acidified to give an excess of 1 per cent. of hydrochloric acid. The solution is adjusted to a volume of 10 ml., and saturated with hydrogen sulphide, the containing tube being first heated in boiling water (10 minutes), and then placed in cold water (5 minutes) during the passing of the gas; the tube is stoppered and kept overnight. The liquid is centrifuged, and the precipitate is washed by centrifuging and decantation with 2 ml. of hydrogen sulphide water containing 1 per cent. of hydrochloric acid. The copper sulphide is dissolved in 4 drops of fuming nitric acid in the tube, which is then heated in boiling water for 10 minutes. After cooling, 5 ml. of water and a slight excess of ammonia are added, and the liquid is diluted to 10 ml. *Micro-electrolysis method.*—The milk-ash is dissolved, as far as possible, in the minimum amount of nitric acid (1 : 1); the solution is centrifuged to remove any residue, and is finally diluted to 6 to 10 ml. The copper is deposited electrolytically by a method similar to that of Pregl ("*Quantitative Organic Microanalysis,*" 1930). The deposited copper is dissolved off the platinum cathode in 1 ml. of nitric acid (1 : 1), and the solution is rendered slightly ammoniacal and diluted to 10 ml. *Colorimetric determination.*—To an aliquot part of the clear copper solution obtained as described above, containing 0·001 to 0·005 mg. of copper, are added 2 ml. of ammonia (strength not stated), and the volume is brought to 10 ml.; 1 ml. of aqueous sodium diethyl dithiocarbamate solution (0·1 per cent.) is added. The yellow colour is immediately compared colorimetrically with a set of 9 standards covering the range from 0·001 to 0·005 with intervals of 0·0005 mg. of copper, prepared in a similar manner from copper sulphate solution. Stress is laid upon the point that throughout the course of the method, vessels, reagents and distilled water free from contamination with copper should be used. Tests on milks containing added copper gave good results. *Results.*—The copper-content of uncontaminated raw milk was found to range from 0·051 to 0·132 p.p.m., with an average of 0·077 p.p.m. for 18 samples. The copper in 7 samples of pasteurised milk varied from 0·088 to 0·741 p.p.m., and in 5 samples of dried milk from 1·37 to 17·15 p.p.m. During the manufacture of milk powder, milk exposed to copper equipment takes up considerable amounts of the metal. S. G. C.

Pink Stains in Cheeses. J. Keilling. (*Ann. Falsif.*, 1935, **27**, 600–602.)—From time to time there appear on certain cheeses, first on the surface and subsequently in the superficial layers, irregularly distributed pink stains (*le rouge des tablards*), accompanied by a bitter taste, with formation of gaseous bubbles. The stains were found to be due to a surface-infection of nitrate, which penetrated the cheese and was denitrified by the superficial bacteria, the resulting nitrite giving rise to a pink colour in contact with the cheese mass. If sterile nitrate is brought into contact with sterile cheese, no stain results, but a fragment of cheese to which a few ml. of a dilute solution of sodium nitrate were added developed within 36 to

48 hours a pink colour which progressively penetrated the cheese and was accompanied by the formation of gas. In the course of a few days a positive reaction for nitrite was obtained. D. G. H.

Test for Distinguishing between Meat Extract and Yeast Extract. R. O. Blench. (*Chem. and Ind.*, 1935, **54**, 148.)—About 10 g. of the sample are digested in a mortar with 20 ml. of a 70 per cent. aqueous solution of acetone, the yellow supernatant liquid is decanted on to a filter, and the clear filtrate is tested as follows: To 3 ml. of the filtrate are added a few drops of strong bromine water, which causes the colour to darken. (If an excess of bromine is added, the dark colour disappears, and is not restored by reducing agents.) With yeast extract a dark red colour develops after 5 minutes, 2 ml. of chloroform are then added, and the mixture is shaken. The chloroform layer which separates on standing has a deep reddish-violet colour. This test was applied to commercial yeast extracts and to an experimental extract prepared in the laboratory from air-dried brewer's yeast; in every instance the same result was obtained. Several of the well-known meat extracts were then submitted to the test, but none gave the reaction, which may possibly be due to tryptophan. Good results were obtained with mixtures of yeast extract and meat extract; 15 per cent. of yeast extract could be easily detected, and a faint reaction was observed with a mixture containing 10 per cent. In testing mixtures containing only a small proportion of yeast extract very little bromine must be added. Similar acetone extracts of egg-yolk and of the fat-free portion of cheese gave a pink colour with bromine.

Diastase in Mixtures of Artificial and Natural Honeys. E. Waltzinger. (*Z. Unters. Lebensm.*, 1935, **69**, 77–79.)—The lack of diastase in these mixtures is attributed to the fact that the acid used in the manufacture of the artificial honey is not neutralised, honey diastase being particularly sensitive to acid. In a factory visited, the artificial honey was produced by heating sucrose to 90° C. with tartaric acid in a concentration of 0·22 per cent. This amount of acid, which was left wholly un-neutralised, was patently sufficient to attack the tinning of the inversion vessel and, although not great enough to bring the acidity of the product above the permissible maximum, proved adequate to destroy the diastase of the natural honey subsequently admixed. T. H. P.

Content of Chlorides, Calcium and Magnesium in the Cocoa Nib. J. Grossfeld and E. Lindemann. (*Z. Unters. Lebensm.*, 1935, **69**, 45–50.)—The percentage chloride, calcium, magnesium, and phosphoric acid contents of cocoa beans and nibs and bulk cocoa have been determined, with the following results: Cl (11 samples), 0·030 ± 0·007 or NaCl, 0·050 ± 0·009; Ca (15 samples), 0·075 ± 0·018 or CaO, 0·11 ± 0·03; Mg (3 samples of nibs), 0·29 ± 0·01 or MgO, 0·48 ± 0·02; P_2O_5 (3 samples of nibs), 1·05 ± 0·05 or PO_4, 1·41 ± 0·08. The chloride was determined by extracting the ash with 0·05 *N* sulphuric acid, clearing the solution with potassium ferrocyanide and zinc acetate, and titrating with 0·01 *N* mercuric nitrate solution in presence of sodium nitroprusside. The titration was carried out in a darkened room, and the liquid was illuminated from the side with a microscope lamp or the like, so that the initial appearance of the Tyndall effect produced by a slight excess of the mercury solution could be observed. T. H. P.

Differentiation of Expressed Cocoa Butter from that Extracted with Solvents. A. Castiglioni. (*Ann. Falsif.*, 1935, **28**, 24–27.)—Since the physical constants of these two types of butter may be very similar, and since Aufrecht's test (ANALYST, 1929, **54**, 346) may sometimes give misleading results according to the nature of the manufacturing process and to the amount of shell present in the raw material, additional tests are desirable. Schmandt's method (*Z. angew. Chem.*, 1929, **42**, 1039) has therefore been adapted to these products, 0·5 to 1 g. of the fat being melted in a test-tube and shaken with 3 ml. of glacial acetic acid. When the acid layer has separated it is observed in filtered ultra-violet light, a bright green-yellow fluorescence being obtained with solvent-extracted products, and no colour with expressed cocoa butters. Molin's antipyrine test (*Pharm. Zeit.*, 1904, **49**, 925) has also been adapted for the purpose, a mixture of 0·5 g. of cocoa butter, 2 ml. of 95 per cent. alcohol, 3 ml. of hydrochloric acid (*d.* 1·19) and a few crystals of antipyrine being boiled and allowed to cool. The liquid layer develops a red colour which is apparent in the presence of 0·2 g. of solvent-extracted fat. (In the analogous reaction, which may be used as a test either for antipyrine or for vanillin, the above procedure is followed, the cocoa butter being replaced by the vanillin and the alcohol being finally removed on the water-bath; an orange-yellow colour shows a positive reaction.) These reactions are not given by the usual adulterants of cocoa butter (*e.g.* coconut oil and palm oil). Morawsky's test for solvent-extracted and expressed olive oils (*cf.* Fachini, *Giorn. Chim. Indust. Applic.*, 1926, **8**, 174, 428) may also be applied to cocoa butter, 0·5 g. being warmed with 3 ml. of acetic anhydride. A drop of sulphuric acid (*d* 1·53) is then added to the filtrate from the cooled liquid, when solvent-extracted products give a fugitive violet colour changing to pale green, whilst expressed butters do not give the intermediate violet shade, but turn green immediately. J. G.

Seed Oil of the Bael Fruit Tree (*Aegle Marmelos*, Corr.). R. Child. (*J. Amer. Chem. Soc.*, 1935, **57**, 356–357.)—The fruit of the Bael or Beli tree, *Aegle Marmelos*, Corr. (Nat. Ord. *Rutaceae*), is used in India for the treatment of dysentery. Nine fruits yielded 200 seeds of average weight 0·118 g. and containing 23·5 per cent. of shell and 76·5 per cent. of kernel. The kernels contained 8·35 per cent. of moisture and 45·0 per cent. of oil. The colourless clear oil, which had a faint odour of linseed, gave the following values:—Sp.gr. 30/4° C., 0·918; n_D^{40}, 1·4647; dispersive power ω, 0·0202; saponification value, (i) 193·6, (ii) 196·7; iodine value (Wijs), (i) 108·0, (ii) 107·1; free fatty acids (as oleic acid), (i) 0·42, (ii) 1·26 per cent.; unsaponifiable matter, 1·58 per cent.; thiocyanogen value, 24 hours, 70·4; Hehner value, 93·7; saturated acids (corr.), 23·9 per cent. The approximate composition of the first sample was: Palmitic, 15·6; stearic, 8·3; oleic, 28·7; linoleic, 33·8; and linolenic acid, 7·6; glyceryl (C_3H_2), 4·4; and unsaponifiable matter, 1·6 per cent. These constants are very similar to those of other oils of the *Rutaceae* family (*Calodendron capense*, *Limonia Warneckii*, *Citrus limonum* and *C. aurantium*). The non-fatty residue of the kernels is very rich in nitrogen, containing about 70 per cent. of protein.

D. G. H.

Quantitative Determination of Powdered Linseed. H. Saber. (*Quart. J. Pharm.*, **1934, 7, 645–653.**)—Linseed possesses a well marked sclerenchymatous layer, one cell thick, which may be readily identified in the powder, and the method for determining the quantity of linseed present in a powder is based on the area per g. of the sclerenchymatous tissue present. To determine this area about 10 g. of the seeds are first defatted, and the amount of oil present in the dried sample is determined. Four g. of the defatted residue are reduced to No. 85 powder, and 0·1 g. is thoroughly mixed with 0·05 g. of lycopodium spores, and rubbed to a smooth paste with 1 ml. of 0·1 per cent. phloroglucinol solution in alcohol. The solution is left to evaporate almost to dryness, and 1 ml. of concentrated hydrochloric acid is added, a few drops at a time, to the residue, with rubbing after each addition, after which a few drops of glycerin and 1 ml. of chloral hydrate solution (5 : 2) are incorporated, and the preparation is made up to about 10 ml. with a suspending liquid consisting of 2 vols. of glycerin, 1 vol. of tragacanth mucilage, and 2 vols. of water. One drop of the mixture is removed to a microscope slide by means of a tube of 2 to 3 mm. bore, and the area of the particles from the sclerenchymatous layer is determined in comparison with the number of lycopodium spores, as for the epidermis of a leaf (Wallis and Saber, *Quart. J. Pharm.*, 1933, **6**, 655). The mean result for a sample of linseed 40 years old was 34·38 sq.cm. per g. of the sample dried at 100° C., and 49·7 for the fat-free dry sample, and for a sample of fresh linseed, 30 and 50·9 sq.cm., respectively. Variations of the area of the sclerenchymatous layer for individual seeds per g. were from 26·7 to 58·7 sq.cm., the mean value being taken as 37·7. The examination of 10 samples from plants cultivated in different districts and obtained from different sources showed a considerable range in size of seed, but samples grown under similar environmental conditions possessed almost the same quantitative characteristics (size, and area of sclerenchymatous layer). Differences in the conditions of environment affect the area of the sclerenchymatous layer per g. to the extent of 15 per cent. of the mean value, and the degree of variation is not altered by drying or by defatting the seeds. This degree of variation is identical with that due to similar causes observed in the epidermal area results for a number of leaf samples of the same species. The application of the method of procedure to the determination of the proportion of linseed in mixed cakes is given in detail; a mixed cake of linseed, soya-bean, and pea flour, containing 12 per cent. of linseed, gave an experimental figure of 11·7 per cent. D. G. H.

Volatile Oil of Yarrow (*Achillea Millefolium*, Linne.) R. L. McMurray. (*Amer. J. Pharm.*, 1935, **107**, 33–34.)—Steam-distillation of a quantity of yarrow yielded 235 ml. of an oil of intense blue colour, having sp.gr. at 25° C., 0·9066; n_D^{25}, 1·4703; and $[\alpha]_D$, −14·11°. The $[\alpha]_D$ was determined in 95 per cent. alcoholic solution in a 50-mm. tube, and the results agreed with the value obtained by Aubert (*J. Amer. Chem. Soc.*, 1902, **24**, 778), but not with that of Haensel (*Haensels Bericht*, 1901, **4**, 25). The earliest record of the production of a blue volatile oil from yarrow is that of F. Hoffman in 1719 (*De Millefolio*, German Ed., Schaaf-Garben). D. G. H.

Identification of Gum Arabic. I. C. Ritsema. (*Pharm. Weekblad*, 1935, 72, 105–106.)—The following tests (of which the first three were adapted from those of the Dutch Pharmacopoeia and are sensitive to 1 part in 5) were applied to solutions of a number of specimens of gum arabic of satisfactory external appearance, although it is not certain that they were all derived from *Acacia Senegal*:—Ferric chloride solution gave a brown gel which dispersed when shaken. A saturated solution of borax or borax powder gave a white gel which dispersed on shaking. Alcohol gave no gel, but a white precipitate which disappeared on shaking. Basic lead acetate solution gave a white precipitate; the reaction is sensitive to 1 part in 10,000, although it is desirable to make a comparison with a blank test, as the precipitate takes a little time to appear. If to 5 ml. of a 5 per cent. solution of the sample are added a little benzidine and 1 drop of a 3 per cent. solution of hydrogen peroxide, "benzidine blue" is obtained after 1 minute. The preparation of the solution and the reaction should be carried out in the cold, as the peroxidase responsible for the reaction is destroyed at a temperature of 50 to 60° C. Although it is stated that the peroxidase content of gum arabic decreases on ageing, samples which had been in the possession of the author for several years gave stronger reactions than purchased commercial samples. J. G.

Titration of Barbital with Silver Nitrate by the Method of H. Budde. J. M. A. Hegland. (*Pharm. Weekblad*, 1935, 72, 128–129.)—The author prefers this method (cf. *id.*, 1934, 71, 1019) to the alkalimetric (Dutch Pharmacopoeia) method, as it avoids errors inherent in the observation of a change in colour, especially when the sample is originally coloured. The sample (200 to 230 mg.) is dissolved in a solution of 1 g. of anhydrous sodium carbonate in 30 g. of water, and titrated with 0·1 *N* silver nitrate solution, a drop at a time and with continuous shaking, until a permanent faint opalescence results. The end-point is best observed against a dark ground, and is confirmed by the production of a heavy precipitate by the first drop of reagent in excess. The method was compared with the Pharmacopoeia method, 0·1 *N* sulphuric acid being used instead of hydrochloric acid for the titration of salts of barbital. Mean results in ml. of 0·1 *N* alkali and silver nitrate, respectively, are:—Luminal verum, 9·7, 9·65; Dial verum, 9·6, 10·0; Luminal loco, 9·7, 9·93; Dial loco, 9·90, 10·00; Medinal loco, 9·4 (ml. of 0·1 *N* sulphuric acid), 10·7. J. G.

Auto-oxidation of Ether. M. Landon. (*Bull. Soc. Chim.*, 1935, 2, 53–57.)—Although ether tends to undergo auto-oxidation, with the formation of peroxides, even in the dark, this reaction is very much more rapid in the presence of light. The formation of peroxides is accelerated by the presence of aldehydes, but is retarded by water and especially by acids; alkalis hinder the appearance of oxidation products. The action of ultra-violet light was not studied, as the rise in temperature due to the incidence of the rays becomes more important than any oxidation which might take place. The nature of the container is important. For storage purposes, ether should be kept in the dark and be free from aldehydes, but it is difficult to keep pure ether except in the presence of sodium, which reduces any oxidation product as soon as it is formed. For the removal of peroxides from ether, treatment with sodium hydroxide, followed by distillation, is recommended. S. G. S.

Determination of Peroxides in Ether. M. Landon. (*Bull. Soc. Chim.*, 1935, 2, 34–53.)—Two methods of determination of peroxides in ether are suggested, one being titration with *N*/10 potassium permanganate solution, and the other titration of the iodine liberated from potassium iodide solution. The titration with potassium permanganate in the presence of sulphuric acid is quantitative, but gives the total peroxide and does not distinguish between free peroxide (hydrogen peroxide) and combined peroxide (ethyl peroxide). Since the amount of iodine liberated from potassium iodide is a function of the time allowed for the reaction, it does not give a quantitative result, but it does allow the difference between the free and combined peroxide to be determined. The ether (20 ml.) is mixed with 2 ml. of 10 per cent. potassium iodide solution, shaken continuously for 5 minutes, and then titrated with *N*/100 sodium thiosulphate solution. The determination is then repeated, shaking for 20 minutes. If the first result exceeds the second, the ether contains a large amount of free peroxide; but, if the reverse is the case, most of the peroxide is in the combined form. If the ether is acid in reaction, this method is useless, and, in any case, an isolated result is of no absolute value, but is only comparative. Ether which has been exposed to light for any length of time will contain most of the peroxide as hydrogen peroxide, and a permanganate titration is indicated. The presence of nitrites and their effect on the result of these titrations must not be overlooked, and Ilosvay's reaction should always be tried. S. G. S.

Occurrence of Resins in Tobacco Smoke. A. Wenusch. (*Z. Unters. Lebensm.*, 1935, 69, 81–85.)—A large proportion of the solid components of tobacco smoke consists of a mixture of a neutral resin, an essential oil, and various resin acids. Whether the resin and resin acids of the smoke are chemically identical with the resinous compounds of the original tobacco has not yet been decided. The smoke from 350 cigarettes, corresponding with about 300 g. of tobacco actually smoked, yielded: 0·4 g. of resin acid soluble in ether and precipitable by lead acetate in alcoholic solution; 1·4 g. of resin acid soluble in ether, but not precipitable by lead acetate in alcoholic solution; 2·2 g. of resin acid insoluble in ether; 2·7 g. of unsaponifiable resin soluble in ether, and 0·5 g. of oil volatile in a current of steam. T. H. P.

Constituents of Derris Resin. R. S. Cahn and J. J. Boam. (*J. Soc. Chem. Ind.*, 1935, 54, 42–45T.)—Although those derris resins which contain only small amounts of rotenone (designated "Sumatra type") yield, on treatment with alkali, 50 to 60 per cent. of crude toxicarol, it is shown that the toxicarol is not present as such in the resin. A new dimorphic substance of insecticidal properties, undoubtedly occurring free, has been isolated from Sumatra type of root by simple crystallisation. The carbon tetrachloride solution of the resin, when kept for long periods, deposited a gradually increasing yield of crystals (5 per cent. in 2 weeks), and these, on fractional extraction with alcohol, yielded 1·8 per cent. of pure rotenone and 0·55 per cent. of a new individual substance (m.p. 189° C.). If crystallised from acetone, however, the substance melted at 192° to 194° C., reverting to the first form when kept in a vacuum desiccator or dissolved in other solvents. The probable formula is $C_{23}H_{22}O_7$, and the substance differs from isomeric tephrosin in being phenolic and not readily losing the elements of water, and from the isomeric toxicarol in being colourless. It appears that *dl*-toxicarol, and at least part of the *dl*-deguelin, do not occur as such in the resins, nor does more than a small amount of tephrosin (either optically active or inactive), whilst deguelin occurs, at least partly, as the *l*-form or as a single derivative or precursor thereof. The remaining deguelin and tephrosin occur in some form of combination or as simply related precursors, and nothing is known as to the mode of combination of the toxicarol, but it is unlikely that large amounts of simple esters of the *dl*-form are present. The preparation of toxicarol, acetyl rotenone, dehydrodeguelin and certain esters is described. The esters of toxicarol are readily hydrolysed by acid, and since derris resins which yield at least 40 per cent. of toxicarol with alkali do not yield it with acid, it is concluded that esters of *dl*-toxicarol are absent from such resins. The conclusion that the value of a derris root or resin can be assessed only by the rotenone-content is quite unjustified, and, since deguelin, tephrosin and toxicarol do not occur as such in the root (or occur only in very small quantities), data as to their relative toxicities are inapplicable to assessment of the root. D. G. H.

Determination of Rotenone in Derris Root and Resin. R. S. Cahn and J. J. Boam. (*J. Soc. Chem. Ind.*, 1935, **54**, 37–42T.)—The toxicity of derris root is due to a mixture of compounds obtained as a resin by extraction with various organic solvents; from the solution of this resin in carbon tetrachloride a crystalline "complex" rotenone separates. Certain modifications in the carbon tetrachloride method of determining rotenone are suggested, but, even in the modified form, low results are obtained if the resin contains less than about 17 per cent. of rotenone, and with very small amounts the method fails, owing to the phenomenon of "hidden" rotenone, *i.e.* rotenone that can be determined only when special methods are adopted, possibly owing to the presence of an inhibitor of crystallisation. For the determination, the derris root should pass entirely through a 50-mesh sieve before sampling, and should be dried in a vacuum desiccator until not more than 5 per cent. of moisture remains. Enough of the powdered root is taken to yield 5 to 10 g. of extract to trichloroethylene in 8 hours, the solvent being changed after 4 hours, and if the second solution acquires more than a very pale yellow colour a further extraction is carried out with another quantity of solvent. The combined solutions of extract are evaporated until thickening occurs and bubbling begins, when a gentle current of air is blown into the flask, which is rotated over a naked flame until the odour of hot derris resin is apparent. The flask is weighed and the resin rapidly dissolved in 2 parts of warm carbon tetrachloride saturated with rotenone (x g. of resin, $2x$ ml. of CCl_4), cooled, seeded if necessary, and kept overnight. The crystals are collected, with the aid of the water-pump, on a disc of Whatman No. 1 (not hardened) filter-paper, washed with the saturated carbon tetrachloride until the filtrate is nearly colourless, and dried to constant weight in air below 50° C. The weight of the complex, multiplied by 0·72, gives the weight of rotenone. Total extract is determined by evaporating the trichloroethylene solution to dryness, and heating the residue until constant in weight in an oven at 100° C. To detect "hidden" rotenone, 1 g. of rotenone and 4 g. of the resin are dissolved in 10 ml. of carbon tetrachloride saturated with rotenone, and the solution is kept overnight and then treated as described above. The rotenone carbon tetrachloride crystals, which separate in the determination, are at best only 90 to 95 per cent. pure, and probably not more than 80 to 90 per cent.; their purity may be determined by stirring the complex in 5 parts of alcohol and leaving the solution overnight, when solvent-free rotenone crystallises out. The percentage yield, which is termed the percentage alcohol recovery, is regarded as the best indication of purity. D. G. H.

Biochemical

New Method for the Determination of the Acid-Base Balance in Food Materials. J. Davidson and J. A. Le Clerc. (*J. Biol. Chem.*, 1935, **108**, 337–347.)—The acid-base balance in a food material is generally determined by computations based on its content of the acid-forming elements, phosphorus, sulphur, and chlorine, and the base-forming elements, potassium, sodium, calcium, and magnesium. The quantities of these elements in the food are converted into ml. of normality values, and the difference between the sum of the acid values and the sum of the base values is the base balance or the acid balance, as the case may be. When the mineral analysis of the food is not an object in itself, this procedure is lengthy, and, in addition, is liable to certain errors. The question whether phosphorus should be considered bivalent or tervalent is a vexed one, and losses of chlorine, sulphur, etc., during ashing may give false results. The suggested procedure is based on the direct titration of the ash, with corrections for sulphur and chlorine lost during the combustion. The requisite amount of material is ashed in a platinum dish at 550° C. The ash is dissolved in an excess of 0·5 *N* acid, and is titrated back with 0·1 *N* alkali. Sulphur and chlorine are also determined on the original material, with and without means of preventing losses—magnesium nitrate being used to prevent the loss of sulphur, and sodium carbonate the loss of chlorine. The differences between the results of the two respective determinations of sulphur and chlorine are the quantities of these elements lost during combustion. These losses are converted into "normal" acid values, and subtracted from, or added to, the titration values, according to whether it is a base or an acid balance. The use of phenol red or any indicator that registers the exact neutral point (*p*H 7·0) is proposed in place of the commonly used methyl red or phenolphthalein.
S. G. S.

Nutritive Value of the Fatty Acids of Lard and some of their Esters. S. Lepkovsky, R. A. Ouer and H. M. Evans. (*J. Biol. Chem.*, 1935, **108**, 431–438.)—The fatty acids were isolated from lard by the usual saponification procedure. They were then distilled and esterified with glycerin to form a "synthetic" lard. For the normal growth of rats the synthetic product is just as satisfactory as the natural one, when fed in the proportion of 25 or 60 per cent. of the diet. The free fatty acids, both alone and with the addition of glycerin, were good sources of energy when fed as 25 per cent. of the diet, but were inferior to the glyceride at the 60 per cent. level. The methyl and ethyl esters were also good on the 25 per cent. basis, but on the 60 per cent. basis the methyl esters gave poor growth, whilst with the ethyl esters an initial mortality was followed by a fair growth of the survivors. Propylene glycol was the best of the dihydric alcohols, ethylene and diethylene glycols, both being poor and causing serious lesions in the kidneys of the experimental animals. S. G. S.

Determination of Iodine in Blood and Thyroid. I. Bellucci and R. Vigni (*Gazz. Chim. Ital.*, 1934, **64**, 634–643.)—With careful working, the organic matter of blood or thyroid may be completely destroyed by treatment with potassium hydroxide, without loss of iodine. From 10 to 15 grms. of blood, treated with a very small amount of potassium oxalate as an anti-coagulant, are weighed in a nickel dish (8 to 10 cm. wide and 4 to 5 cm. high) and mixed, by means of a thin nickel rod, with 0·25 g. of potassium hydroxide in concentrated, boiling solution. The dish is then gently heated on an asbestos gauze over a ring burner 3 cm. across, the mass being kept stirred until a black, spongy residue is obtained. Heating and stirring are then continued over the naked flame as long as vapours are emitted. When the dish has cooled, the mass is moistened and mixed with 5 ml. of 6 per cent. hydrogen peroxide solution rendered faintly alkaline with potassium hydroxide. After 10 or 15 minutes, the dish is carefully heated, first on the asbestos gauze and later over a naked flame, the mass being stirred until a uniform, gray ash remains. This is treated with 10 ml. of the hydrogen peroxide solution and the heating is repeated. The ash is next moistened with water, scraped to the bottom of the dish, dried by heating on the gauze and finally heated for 15 to 20 minutes over a naked flame. The whitish residue is extracted three times with 8 to 10 ml. quantities of boiling water, the extracts being filtered through an 8 cm. filter (Schleicher and Schüll N. 589/2), on which the whole ash is ultimately washed. The filter and residue are returned to the dish, moistened with a few drops of concentrated potassium hydroxide solution, and incinerated as before. The combined filtrates and washings are next transferred to the dish and the whole is evaporated to dryness on the gauze and afterwards heated for about 5 minutes over the bare flame.

After being moistened with water, the ash is ground by means of a small agate or glass pestle with three small quantities (3 to 4 ml.) of 95 per cent. alcohol, the alcoholic extracts being decanted into a small porcelain dish and evaporated to dryness on a water-bath. The residue is taken up in water and transferred to a small beaker so as to give 10 or 15 ml. of solution containing the iodine as potassium iodide. This is oxidised to iodate by heating the liquid to incipient boiling for 3 to 4 minutes with a few drops of dilute potassium hydroxide and a few crystals of potassium permanganate, excess of which is then destroyed by adding a few drops of strong alcohol to the hot solution. Any separated manganese dioxide is removed by filtration, the filtrate and washings being evaporated to 6 or 7 ml. Traces of nitrite present are destroyed by boiling the liquid gently for 3 or 4 minutes with 0·5 to 1 ml. of glacial acetic acid and 0·1 g. of urea. The cooled solution is shaken with a few cg. of potassium iodide and a few drops each of dilute (1:4) sulphuric acid and carbon disulphide. The iodine is then determined by titration with 0·002 N sodium thiosulphate solution (run in from a micro-burette) until the amethyst colour of the carbon disulphide solution of the iodine just disappears.

Fresh thyroid is freed from fat and surrounding connective tissue and is cut into thin slices which are spread on a clock-glass and dried to constant weight in a vacuum over sulphuric acid. The dry material is powdered in a mortar and 0·5 to 1 g. is treated with 0·5 g. of potassium hydroxide. The subsequent procedure is as described above, except that the final volume of the solution may be increased to 10 to 15 ml., which is titrated with 0·004 N thiosulphate.

Test experiments with sucrose to which about 10γ of iodine were added gave satisfactory results. Two samples of blood taken a few days apart from a normal individual showed, respectively, 9·86 and 10·7γ per 100 g. Other results were: Patient, just convalescing after pulmonitis, 183γ; patient suffering from genital adipose dystrophia, 135γ. A human thyroid, having the abnormal weight 60 g. (fresh), contained 72·8 mg. of iodine per 100 g. of dry matter (*cf.* Abst., p. 275).

T. H. P.

Effective Method of Extracting Vitamin B_1. S. Itter, E. R. Orent and E. V. McCollum. (*J. Biol. Chem.*, 1935, **108**, 571–577.)—Extraction of vitamin B_1 from yeast by means of gaseous hydrogen chloride in the presence of methyl alcohol has been found to be more effective than extraction with aqueous hydrochloric acid. The dried yeast (100 g.) is suspended in 50 ml. of absolute methyl alcohol, and into this mixture is passed a stream of dry gaseous hydrogen chloride until a concentration of approximately 4 N is attained. The acidified mixture is allowed to stand overnight and then filtered through a Buchner funnel. The residue is washed with 200 ml. of absolute methyl alcohol, and the washings and filtrate are evaporated *in vacuo* to a thick syrup. Biological tests indicated that the residues contain no vitamins B_1 or B_2, but that the extract is as active, in proportion, as the original yeast. The extract is also unusually low in alkaline elements and provides a good source of vitamin B_1 for inorganic deficiency studies.

S. G. S.

Quantitative Determination of Ascorbic Acid. (Vitamin C). H. Tauber and I. S. Kleiner. (*J. Biol. Chem.*, **1935**, **108**, **563–570**.)—The reducing action of ascorbic acid on acid ferricyanide solution has been made the basis of a colorimetric method of determining vitamin C. To remove interfering substances, about 20 g. of the material are ground up with acid-washed sand in the presence of hot 8 per cent. acetic acid, a total volume of 100 ml. being used. The combined extracts are centrifuged and filtered if necessary. To 50 ml. of the extract 15 ml. of a 20 per cent. solution of mercuric acetate are added, and the reaction to Congo-red is adjusted, if required, with calcium carbonate until it is only slightly acid. The solution is again centrifuged and filtered if necessary. If, on testing with mercuric acetate, a precipitate still forms, this treatment must be repeated, but, if no precipitate is produced, the mercury is removed from the filtrate by passing hydrogen sulphide through the solution. When the mercuric sulphide has been filtered off the hydrogen sulphide must be removed, after the vessel has stood overnight, by bubbling nitrogen through the liquid. If it is desired to omit this preliminary treatment, the material under investigation is ground up with sand and 10 per cent. trichloroacetic acid for animal tissue, or hot 8 per cent. acetic acid for plant tissue. At least three extractions should be made, a total of 20 ml. of acid being used for each 10 g. of material, and the liquid decanted each time. The combined extracts are then centrifuged at high speed, and the clear liquid is diluted to a definite volume with the respective acid and filtered, if necessary. To 5 ml. of the clear fluid 2 ml. of the ferricyanide solution are added, and to 1 ml. of the standard ascorbic acid solution are added 4 ml. of the requisite acid and 2 ml. of the ferricyanide solution. Rubber stoppers are inserted in the tubes, the contents are well mixed, and the tubes are placed in a water-bath at 40° C. for 3 minutes. The contents of the tubes are then cooled, and 5 ml. of the ferric gum solution are added. The blue colour develops quickly, and the colorimetric determination may be made immediately with a yellow light filter (*cf.* Folin and Malmros, *J. Biol. Chem.*, 1929, **83**, 115). The potassium ferricyanide solution is an aqueous one of 0·4 per cent. strength. The ferric gum solution is prepared by suspending, on a copper wire screen, 20 g. of soluble gum ghatti in 1 l. of water for 18 to 36 hours. The screen is then removed and sedimentation is allowed to take place. After decantation or filtration, 5 g. of anhydrous ferric sulphate dissolved in 75 ml. of 85 per cent. phosphoric acid plus 100 ml. of water, are added to the gum solution. To the mixture are then added, in small portions, about 15 ml. of 1 per cent. potassium permanganate solution, to oxidise reducing substances in the gum and possible traces of ferrous iron in the ferric sulphate. After 24 hours at room temperature the solution is clear and ready for use. The standard solution of ascorbic acid is prepared by dissolving 25 mg. of pure ascorbic acid and 50 mg. of pure cystine in 90 ml. of boiling 0·01 *N* hydrochloric acid solution. After cooling, this solution is diluted to 100 ml. with water. Cystine is used to inhibit the auto-oxidation of the ascorbic acid, which would occur rapidly in its absence, but the solution prepared as described will last for one day.

S. G. S.

Determination of the Common Carotenoids and Analyses of Carotene and Leaf Xanthophyll in Thirteen Plant Tissues. E. S. Miller. (*J. Amer. Chem. Soc.*, 1935, **57**, 347–349.)—The Willstätter and Stoll methanol-ligroin (89 and 92 per cent.) partition method (*Untersuchungen über Chlorophyll*, Berlin, 1913) was found to be quantitative only when corrected. A new method for the extraction of the carotenoids was devised, from 1 to 10 g. of green (or 0·05 to 0·5 g. of dry) samples of various grasses and sugar-cane hybrids being used. The samples are macerated with 25 ml. of acetone and 25 g. of quartz sand, and to the extract are added 20 ml. of 95 per cent. ethanol saturated with potassium hydroxide. Alternate maceration and extraction are repeated three times with 25-ml. portions of acetone, and then twice with 35 ml. of ether, and the extraction of the pulp and sand with ether is completed in a Soxhlet extractor on the water-bath. The combined extracts are shaken gently with 1·5 l. of water, and the water is separated. If saponification is not complete, a further 10 ml. of ethanol (saturated with potassium hydroxide) are added, extraction is carried out with

100 ml. of ether, and the washings are added to the former washings. The ethereal extracts are washed 4 times with 500-ml. portions of water, the funnel being left for 3 to 4 minutes (5 to 8 minutes for the final washing) before the aqueous washings are drawn off. The ethereal solution (150–200 ml.) is evaporated *in vacuo* to 50 to 60 ml., measured and made up to 100 ml., and analysed the same day. Analysis by the Willstätter and Stoll partition method showed that the 13 plant samples contained either no α-carotene or less than 0·7 per cent. The following results are the averages (in parts per million) of determinations on duplicate samples:

	Total carotenoids	β-carotene	Leaf xanthophyll	Ratio of β-carotene to leaf xanthophy
Hordum sativum	115·4	31·7	84·0	1:2·65
Bromus inermis	285·0	51·3	238·5	1:5·55
Zea mays, L. (Country gentleman)	263·0	46·2	216·3	1:4·68
Zea mays, L. (Golden bantam)	288·5	37·3	221·7	1:3·29
Setaria italica	302·5	83·0	220·5	1:2·65
Sudan grass	445·0	91·1	354·0	1:3·88
Sugar-cane hybrid	478·0	140·0	338·7	1:2·42

D. G. H.

Toxicological

Toxicological Detection of Ergot. H. Kluge. (*Z. Unters. Lebensm.*, 1934, **68**, 645–650.)—For this purpose use is made of: the colouring matter, sklererythrin; the alkaloids, ergotinin, ergotoxin, and ergotamine; and the red colouring matter not precipitated by lead acetate or by subsequent removal of the lead by means of hydrogen sulphide. The material, rendered distinctly acid with 10 per cent. tartaric acid solution, is digested on a water-bath at about 75° C. with about the threefold quantity of 90 per cent. alcohol. The cooled liquid is filtered, and the residue again digested with alcohol, and filtered, the combined filtrates being evaporated in a vacuum. The syrupy residue is mixed with alcohol until precipitation begins and is then poured in a thin stream, with constant swirling, into the five-fold volume of alcohol. After 12 hours the liquid deposits a brown precipitate, which is filtered off. The filtrate is again evaporated in a vacuum to a syrup, which is dissolved in hot water, the solution being then cooled and filtered to remove fat. The aqueous filtrate, acidified with 2 drops of hydrochloric acid, is shaken with three quantities of ether, and the united ethereal extracts are washed with a little water and passed through a small, dry filter (A), giving ethereal extract I. The acid aqueous solution is made alkaline with sodium carbonate solution and again extracted thrice with ether, the ethereal extract (II) being purified as before.

In presence of sklererythrin, filter A shows a delicate cherry-red colour, which changes to violet-red when the filter is moistened with alcohol and exposed to ammonia vapour. The ethereal extract I is transferred to a separating funnel, and 5 ml. of saturated sodium bicarbonate solution are run in to form a lower layer. On gentle swirling, a violet-red ring forms, the colour permeating the whole liquid on shaking. When the alkaline layer is separated, acidified with hydrochloric acid, and shaken with 5 ml. of ether, the ethereal layer shows absorption bands at 527 to 543$m\mu$ and 485 to 507$m\mu$. If the ethereal layer is shaken with 2 ml. of the sodium bicarbonate solution, it shows three absorption bands at 550 to 575, 515 to 530, and 485 to 495$m\mu$, respectively. When material isolated from the stomach or intestines is used, the results of the spectroscopic examination are, however, unsatisfactory. Capillary analysis gives better results: The sodium bicarbonate solution is acidified and shaken with 2 ml. of ether, the ethereal extract being placed in a test-tube containing a narrow strip of filter-paper, which protrudes from the tube. As the ether evaporates, the lower portion of the paper assumes a delicate red colour, which deepens to a stable (for weeks) violet-red under the action of ammonia vapour.

To test for the ergot alkaloids, the ethereal extract II is purified by shaking it with 10 ml. of very dilute hydrochloric acid, making the acid liquid alkaline with sodium bicarbonate, and shaking with ether. The ethereal solution is concentrated at room temperature to about 3 ml., 1 ml. of this being mixed with 1 ml. of glacial acetic acid, and 1 ml. of concentrated sulphuric acid containing a trace (about 0·1 per cent.) of ferric chloride run into the tube to form a layer at the bottom. In presence of ergot alkaloids, a blue inter-layer ring gradually forms and later spreads through the ether layer. The remainder of the ether concentrate is evaporated to dryness, and the residue is dissolved in 1 ml. of concentrated hydrochloric acid and tested by means of the ordinary alkaloid reagents.

Ergot separated from organs requires purification before testing. The hydrochloric acid solution is treated in a centrifuge tube with a few drops of potassium-mercuric iodide solution and centrifuged. The separated precipitate is freed from traces of liquid by means of filter-paper, then digested with excess of anhydrous acetone, and again centrifuged. The clear acetone solution, containing the alkaloids, is treated with very dilute sodium hydroxide solution and shaken three times with ether. The united ethereal extracts are evaporated to dryness, and the residue, taken up in a few ml. of chloroform, is mixed with 2 drops of sodium sulphide solution, 2 drops of sodium carbonate solution, and 1 to 2 ml. of water. The mixture is shaken with two portions of chloroform, evaporation of the filtered chloroform extracts yielding the alkaloids in highly pure state. The reactions of the alkaloids separated from organs are shown only faintly, and hence are only given if relatively large amounts of ergot have been taken. Such separated alkaloids do not respond to pharmacological tests. T. H. P.

Bacteriological

***Polystictus Versicolor.* [Wood-rotting fungus]. B. A. Jay.** (*Kew Bull.*, 1934, No. 10, 1–15.)—*Polystictus versicolor* (L.) Fr., has been the cause of most of the rotting, under damp conditions, of felled hardwoods in Britain; it is the most serious of all wood-rotting fungi which attack the dead wood of broad-leaf trees, and it is the most cosmopolitan species to be found on the sap wood of such trees. It is absent from living trees. The individual sporophores are about 7 cm. wide and 4 cm. deep, and they may be bracket-shaped or resupinate and usually overlap one another on the wood, forming dense masses. The fungus grows vigorously on a medium consisting of 2 per cent. of malt extract and 2 per cent. of agar-agar in water, growth being thicker but slower in the presence of 1 per cent. of malic acid. Slope and plate cultures show a smooth, pale yellow or white, closely-woven mat of felty mycelia, with a tendency to zonation, the disappearance of the brown colour of the medium as growth proceeds being a useful means of identification, although it may be produced by other species. Fruit bodies are absent. The mature hyphae are 3 to 4μ wide, and are hyaline and have a few septa, usually with clamp connections, the tips being swollen and frequently bifurcated. Rhomboidal crystals occur in most cultures. Cultures from different hosts were identical, and the spores retained their vitality in the dry state for at least 3 months. Optimum growth at 23° C. is between *p*H 4·6 and 5·6, there being no growth below 3·0 or above 7·3 (*p*H adjusted with malic acid or potassium hydroxide). The lowest lethal temperature is 60° C. for 15 minutes (*cf.* Cartwright and Findlay, *Ann. Bot.*, 1934, **48**, 481), and the lowest concentration of agar-agar required to produce the maximum rate of growth is 4 per cent.; light has a slight inhibiting effect. Wood blocks are best inoculated by inserting them in Roux tubes containing slope cultures of fungus in which the agar reaches just above the constriction; this enables the wood to be attacked by the fungus, but prevents staining or undue wetting by the medium. The maximum loss in weight recorded was 80 per cent. (for an ash-block) in 4 months. The reaction of the fungus to wood preservatives was tested by shaking various amounts of a sterile solution of the preservative with the medium before plating out. The plates were examined after a week at 23° C. in order to ascertain the approximate lethal concentrations, and the experiments were then repeated, with a more restricted range of concentrations. The minimum concentration to inhibit growth was 0·2 per cent. for sodium fluoride, and 0·05 to 0·1 per cent. for coal-tar creosote B.S.S. Type A used in the form of an emulsion in 20 per cent. gum arabic solution; the lethal concentrations were 0·2 to 0·5 per cent. in both cases, and less than 0·5 per cent. for zinc chloride. Exposure of a plate-culture to the vapour evolved from a pad of filter-paper soaked in formalin and placed in a beaker for 30 minutes, 1 hour and 2 hours, stimulated, inhibited and prevented subsequent growth on 2 per cent. malt slopes, respectively. In order to determine the minimum amount of preservative to prevent growth on a particular wood, blocks of the wood were soaked in various strengths of preservative for 4 hours in a vacuum, and then dried and placed on slope-cultures, and the losses in dry weight were compared with those of controls. Values for sodium fluoride were 0·5 per cent. on beech, 2·0 on ash, over 2·0 on elm, and over 2 per cent. for creosote on beech; the heartwood of oak (*Quercus pedunculata*) was even more resistant. The best methods of prevention of decay are to creosote permanent erections, and to dry felled wood as soon as possible before rot begins; a 4 per cent. solution of sodium fluoride is recommended where creosote cannot be used, but contact with water not only washes this out, but also produces conditions favourable for growth. J. G.

Organic

Acids of Chinese and Esparto Grass Waxes and the Hydrocarbons of Esparto and Candelilla Waxes. F. J. E. Collins. (*J. Soc. Chem. Ind.*, **1935**, **54**, 33–35T.)—*Acids of Chinese Wax.*—In continuation of the work of Francis, Piper and Malkin (*Proc. Roy. Soc.*, 1930, A, **128**, 247), an attempt was made to separate the acid $C_{26}H_{52}O_2$ from the mixture of acids present in the wax, including $C_{28}H_{56}O_2$ and some $C_{24}H_{48}O_2$ and $C_{30}H_{60}O_2$. A prolonged systematic fractional distillation (in a vacuum of 0·5 mm.) of the ethyl esters of the mixed acids resulted in only a partial separation. Tests on the fractions showed that the coincidence of the m.p. of an ester or acid with that of a known synthetic ester or acid may be, and often is, fortuitous, and is therefore, no criterion of purity; the only method of establishing the identity of a pure *n*-fatty acid of high carbon-content is by comparisons of the m.p. and of the *B* and *C* *X*-ray crystal spacings of the acid and ester with the corresponding data for the synthetic compounds (cf. *loc. cit.*). A better separation was obtained by repeated molecular distillation of the ester fractions obtained in the first operation at 10 ^{6}mm. in a constant-temperature still (*cf.* Bruin, *Bur. Stand. J. Res.*, 1929, **2**, 470), the contents of which were stirred by an iron ball kept in motion by an external electro-magnet. Eventually a fraction was obtained which yielded an acid (m.p. 86·5° C.), which crystallised in separate sharp-edged crystals, and control tests on the lines suggested above indicated that it consisted mainly of the acid $C_{26}H_{52}O_2$ with traces of the acids $C_{24}H_{48}O_2$ and $C_{28}H_{56}O_2$. A further extension of this method could be used to obtain the pure acid, but larger quantities of material would be required.

Esparto Grass Wax.—This is a dark brown, hard, brittle material, with m.p. 70° to 74° C.; acid value, 30; saponification value, 75. A mixture of ether and acetone (1 : 2) extracted a brown resinous material which was rejected, the residue being saponified. The solution was evaporated, the hydrocarbons and alcohols present were extracted with hot petroleum spirit, the acids in the residue were liberated from the potassium salts and converted into barium salts, which were washed exhaustively in succession with boiling alcohol, acetone and benzene, and the acids were again liberated and converted into the ethyl esters. These were fractionated in the molecular still, the procedure being similar to that already described. The general conclusion is that the free or combined acids in Chinese wax have, on an average, a lower carbon-content than those in esparto wax, the lowest acid containing 24 and 26 C atoms, respectively; the presence of $C_{32}H_{64}O_2$ and of $C_{34}H_{68}O_2$ in esparto wax was also indicated. *Hydrocarbons from Esparto and Candelilla Waxes.*—Both waxes contain approximately 70 per cent. of a hydrocarbon which has similar properties in the two cases (*cf.* Meyer and Soyka, *Monatsh.*, **1913**, **34**, 1159). The mixture of alcohols and hydrocarbons extracted after saponification (cf. *supra*) was, therefore, acetylated (to prevent dehydration of the alcohols) and distilled in a vacuum of 10^{-3} mm., the distillate being saponified and the resulting product recrystallised repeatedly from a mixture of benzene and alcohol, in which the alcohols are more soluble; further purification was obtained by oxidation on the water-bath with potassium dichromate and glacial acetic acid, followed by treatment with warm concentrated sulphuric acid and crystallisation from benzene. The hydrocarbons from the two sources then appeared identical in all respects, and were composed chiefly of the *n*-paraffin $C_{31}H_{64}$, about 4 per cent. of another hydrocarbon being present in the product derived from esparto. The synthetic hydrocarbon $C_{31}H_{64}$ (*cf.* Chibnall, *Biochem. J.*, 1931, **25**, 2072) has a well-marked transition-point at 62° to 63° C.; a second at 67·4° C.; m.p. 67·5° C.; and resolidifies at 67·2° C. Corresponding figures for the hydrocarbons of esparto wax and candelilla wax, respectively, were:—61° to 61·5° C., 62° to 63° C. (both indefinite); 66·7°, 67·5° C. (both well-defined); 67·7°, 67·8° C.; and 67·4°, 67·4° C. The transition-points were obtained only after treatment with sulphuric acid. So far as is known at present, the acids of waxes of this type are all members of the *n*-aliphatic series, and have an even number of carbon atoms, whilst the hydrocarbons have an odd number of carbon atoms. J. G.

Determination of Selenium in Organic Materials. H. C. Dudley and H. G. Byers. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 3–4.)—Selenium has been found in the tissues, blood, faeces and urine, and also in the milk, of animals which have ingested seleniferous food. The following methods are proposed for the pre-treatment of the materials prior to determination of selenium. Fifty to 100 g. of the material (blood, flesh, eggs, etc.) are covered with 150 to 200 ml. of concentrated nitric acid, and the whole is kept at room temperature for 2 to 3 hours, with occasional stirring; 50 ml. of hydrogen peroxide (30 per cent.) are added, with vigorous stirring if frothing occurs, and the vessel is allowed to stand overnight. The mixture is warmed slowly on a steam-bath until frothing subsides, 50 ml. of hydrogen peroxide and 20 ml. of concentrated sulphuric acid are added; the liquid is evaporated to a paste on a steam-bath, and, after cooling, 100 ml. of hydrobromic acid (45 per cent., containing sufficient bromine to colour it a deep yellow) are added. The mixture is distilled to give 50 to 75 ml. of distillate, in which the selenium may be determined, *e.g.* by the method of Robinson (*id.*, 1934, **6**, 274). For milk samples, 500 to 1000 ml. should be taken; for this, and for other fatty materials, *e.g.* egg yolk, it is desirable to carry out the final evaporation on a hot plate. For urine, the sample may be as large as desired; the residual pasty material, if highly coloured, may be decolorised by a third treatment with hydrogen peroxide. *Clinical test for selenium in urine.*—A 100- to 500-ml. sample is mixed with 25 ml. of concentrated nitric acid and 30 ml. of hydrogen peroxide (30 per cent.), slowly warmed, with stirring, until frothing ceases, and evaporated to dryness; a re-evaporation with 10 ml. of hydrogen peroxide is necessary if the residue is coloured dark yellow; 10 ml. of hydrobromic acid (20 to 25 per cent., coloured yellow with a small drop of bromine) are added. The liquid is filtered into a test-tube, and 0·25 to 0·5 g. of sodium bisulphite, hydroxylamine hydrochloride or hydrazine sulphate is added; it is gently warmed for 15 minutes, and kept for 1 to 3 days. Selenium, if present, precipitates out as a pink powder. As little as 0·05 mg. of selenium, added as sodium selenate, was thus detected in 50 ml. of horse urine. S. G. C.

Indicator Properties of Dinitroaniline Azo Dyestuffs. H. Wenker. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 40–41.)—A range of azo dyestuffs has been prepared, 2, 4- and 2, 6-dinitroaniline and their sulphonic acids being used as diazotisable amines, with 1- and 2-naphthol and their sulphonic acids as azo components, and the couplings being made in dilute sulphuric acid solution. The colour-change points of these dyes in solution were investigated. It was found that (i) only azo components with *para* couplings, *viz.* 1-naphthol, 1, 6-, 1, 7- and 1, 8-naphthol-sulphonic acids, gave indicators of strong colour contrast and relatively narrow *p*H range; (ii) dyes with the nitro groups in the 2, 4- position of the diazo components are preferable to those with the nitro groups in the 2, 6-position, as the former give in alkaline solution bluer and brighter shades, and the latter, redder and duller shades with less colour-contrast; (iii) a few of the new dyes compare well with nitrazine yellow (*Ind. Eng. Chem.*, **1934**, **26**, 350) in colour, intensity and contrast, but are inferior in solubility and narrowness of the *p*H range.

S. G. C.

Determination of Sulphur and Sulphate in Wool. R. T. Mease. (*U.S. Dept. Commerce Research Paper, R.P.* 731.)—Wool protein contains 3 to 4 per cent. of sulphur, probably entirely as cystine. During dyeing and finishing some of this may be converted into sulphates, and these may be increased by absorption of sulphurous or sulphuric acid from the air. The wool is prepared for analysis by washing in a 1 per cent. solution of a neutral soap at 70° C. for 30 minutes, rinsing with distilled water at the same temperature, and then extracting in a Soxhlet extractor for 16 hours with alcohol, followed by 6 hours with ether. The residue is air-dried, rinsed with distilled water at 70° C., and again dried and conditioned at 70° F. and 65 per cent. humidity. The fibres are cut into short lengths and mixed thoroughly. Although the Carius method was used for the determination of total sulphur, the author found that the following method involving the use of an oxygen bomb gave greater accuracy:—About 0·5 g. of the prepared wool is wrapped in filter-paper and bound with pure silk. This is laid on a rectangular piece of filter-paper of such a size that, when laid on top of a platinum crucible, the four corners rest on the rim and support the rest of the paper free from contact with metal. The crucible is placed on the ignition platform of a bomb calorimeter, and about 50 ml. of a 2 per cent. aqueous solution of ammonium carbonate are placed in the bomb with sufficient oxygen to give a pressure of 150 to 180 lbs. per sq. in. The specimen is ignited, and, after standing for 10 minutes, the ammonium carbonate solution is removed and filtered. After acidification the sulphur is precipitated as barium sulphate in the usual way. For the determination of sulphate sulphur the methods studied were (*a*) digestion with potassium hydroxide solution, and (*b*) digestion with concentrated hydrochloric acid, the latter being preferred. About 1 g. of the wool is placed in a Pyrex test-tube, 19 cm. long and of 75 ml. capacity. To this are added 20 ml. of 30 per cent. (by weight of HCl) solution of hydrochloric acid, and the whole is heated in a water-bath until the wool dissolves. The solution is cooled, diluted with an equal volume of water, and filtered. The sulphate in the filtrate is determined in the usual manner.

S. G. S.

Inorganic

Quantitative Determination of Thorium by Means of Picrolonic Acid. F. Hecht and W. Ehrmann. (*Z. anal. Chem.*, **1935**, **100**, 87–98.)—Picrolonic acid produces in thorium solutions a crystalline precipitate which, after attaining constant weight, has the composition $Th(C_{10}H_7N_4O_5)_4.H_2O$, with a thorium factor 0·1782. The precipitant contains 2·64 g. of reagent per l. (ANALYST, 1931, **56**, 833, determination of calcium). The neutral thorium solution should be free from alkali and ammonium salts. If nitric acid is present, the solution is evaporated to dryness, and the residue is taken up with the smallest possible quantity of water (for 0·01 g. thorium), and sufficient acetic acid to provide 2·5 to 3 volumes per cent. of free acid after completion of the precipitation. The liquid is heated, and the precipitant is added, drop by drop, during gentle boiling. When precipitation appears to be complete, the rest of the reagent (0·01 g. of thorium requires 50 ml.) may be added all at once. The solution is cooled for at least an hour in an ice-box, and then filtered through a sintered glass crucible; the precipitate is washed 3 to 4 times with ice-cold water (*i.e.* until the washings are colourless), and dried to constant weight in a current of dust-free air (suction). The time required for drying is from 1 to 3 hours; it is not advisable to determine more than 0·1 g. of metal. Very accurate results are claimed. The procedure is especially suitable for micro-work; it does not provide a means for the separation of thoria from the rare earths. W. R. S.

Determination of Thorium with *o*-Hydroxyquinoline. F. Hecht and W. Ehrmann. (*Z. anal. Chem.*, 1935, **100**, 98–103.)—Thorium is precipitated as the compound $Th(C_9H_6ON)_4.C_9H_7ON$, containing 24·347 per cent. of metal. The solution, free from other precipitable metals, is made faintly ammoniacal, and the precipitate is re-dissolved by dropwise addition of 10 per cent. nitric acid. Sufficient acetic acid is added to provide for 2·5 per cent. acidity in the final bulk. The liquid is heated to gentle boiling and treated, drop by drop, with the reagent (4 g. of the base in 8 g. of glacial acetic acid, diluted to 160 ml.), 6 ml. being required for 0·01 g. of metal. If, after addition of half the quantity of reagent, no precipitate has appeared, strong ammonium acetate solution should be slowly added until the precipitate formed no longer re-dissolves. The remainder of the precipitant is added with gentle boiling throughout the manipulation. The precipitate forms pale red heavy crystals. When precipitation is complete, 5 to 10 ml. of strong ammonium acetate solution are added. The final volume is 30 to 200 ml. for a few mg. to 100 mg. of thorium. When cold, the solution is passed through an air-dry sintered glass crucible, the precipitate is washed with cold or tepid water until the washings are no longer yellow, and the crucible is dried to constant weight by suction in air. Very concordant results are claimed both in macro- and micro-work.

W. R. S.

Volumetric Determination of Arsenic Acid. M. F. Taboury and H. Audidier. (*Bull. Soc. Chim.*, **1934**, **1**, 1570–1578.)—The correct conditions for the iodimetric determination in sulphuric acid solution were ascertained. The arsenate solution (10 ml., 0·0165 to 0·000989 molar with respect to As_2O_5) is treated with 2 ml. of strong sulphuric acid and 0·8 g. of potassium iodide, and heated on the water-bath for 10 minutes. The solution is allowed to cool, and the remaining iodine is exactly eliminated with thiosulphate. The liquid is then treated with an excess of bicarbonate, and the arsenite is titrated in the usual manner with iodine solution. W. R. S.

Determination of Zirconium in Ores by the Selenite-Phosphate Method. S. G. Simpson and W. C. Schumb. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 36.)—Preliminary separation of zirconium by precipitation as selenite followed by precipitation of the element as phosphate from the solution of the selenite precipitate in acid has been previously found satisfactory for the determination of zirconium in steel (*id.*, 1933, **5**, 211). A procedure on these lines has now been applied to ores, and has advantages when thorium is present. The ore is decomposed, and the zirconium is precipitated as selenite (*J. Amer. Chem. Soc.*, 1931, **53**, 921). If thorium is present, the precipitate is extracted with a mixture of 40 ml. of 10 per cent. oxalic acid solution and 12 ml. of 6 *N* hydrochloric acid; the thorium, remaining as oxalate, is filtered off. The filtrate is evaporated with 50 ml. of 18 *N* sulphuric acid to destroy the excess of oxalic acid. If thorium is absent, the zirconium selenite precipitate is dissolved direct in 50 ml. of 18 *N* sulphuric acid. The sulphuric acid solution is diluted to 200 ml., and any precipitated selenium is filtered off. The solution is heated to 50° C., and 20 ml. of 3 per cent. hydrogen peroxide and 50 ml. of a 20 per cent. solution of diammonium phosphate are added. After standing for 2 hours, the precipitate of zirconium phosphate is filtered off, washed with 5 per cent. ammonium nitrate solution, and finally ignited and weighed as ZrP_2O_7. Good results were obtained in tests with synthetic mixtures of zirconium dioxide with varying amounts of felspar, apatite, thoria, ceric oxide and ammonium vanadate. S. G. C.

Determination of Fluorine in Sulphuric Acid and Oleum. H. Spielhaczek. (*Z. anal. Chem.*, 1935, **100**, 184–187.)—The acid to be tested (5 to 10 ml.) is pipetted into a 30- to 50-ml. platinum crucible, which is then covered with a glass test-plate. The acid concentration is increased to 85 or 90 per cent. by addition of pure oleum. The crucible is carefully heated, for 25 minutes with a small, and 5 minutes with the full, flame, fluorine, if present, etching the glass. Very dilute acids must not be treated at once with oleum, but with sulphuric acid first, until strong enough to be miscible with oleum without undue rise in temperature. The glass plates used should be of uniform quality (cut from one window pane), and the softer side should be at once marked for use. They are rubbed with sand and dilute hydrochloric acid, the sand sliding less easily off the softer side. The plates are polished with alcohol before use. The standard scale is prepared from solutions of pure sodium fluoride (10, 1, and 0·1 g. per l.), the standards containing 0·01, 0·005, 0·001, 0·0005, and 0·0001 g. of fluorine. The limit of sensitiveness is 0·01 mg. The acidity of all the solutions is adjusted to 85 or 90 per cent. sulphuric acid. Oleum is tested by diluting with pure 50 per cent. acid to the required acidity, adding a little pure powdered sulphur, and heating to 200° C. for 10 minutes. The sulphur decomposes any fluorosulphonic acid, the slight incrustation of sublimed sulphur not interfering. Before comparison, the glass plates are rinsed, and polished until dry. W. R. S.

Detection of Nitrite with Magdala Red. H. Eichler. (*Z. anal. Chem.*, 1935, **100**, 183–184.)—A solution of 0·05 to 0·1 g. of Magdala red in 100 ml. of glacial acetic or strong formic acid is used. The reagent loses its red fluorescence and strikes a blue colour when treated with nitrite in the solid form or in solution at the ordinary temperature. Large amounts of nitrite may destroy the colour. Nitrate does not react. The test may also be carried out with filter-paper treated on one side with an aqueous suspension of Magdala red. If the prepared paper, which appears grey, is moistened with the solution to be tested, dried, and then moistened with strong acetic or formic acid, it becomes blue by the action of nitrite, otherwise red. W. R. S.

Determination of Ozone in Air. E. Briner and H. Paillard. (*Helv. Chim. Acta*, 1935, **18**, 234–237.)—The efficacy of potassium iodide solution and of mixed arsenite and potassium iodide solution as absorbing agents for ozone in small concentration (0·001 to 3·6 per cent.) has been tested. The absorbing solution was agitated in contact with the gas for periods up to 2 hours. Practically theoretical values were obtained for recovery of ozone when 20 per cent. potassium iodide solution alone was employed, with a 1-hour period of contact. On the other hand, with 0·1 *N* arsenite solution, together with potassium iodide, appreciably low results were obtained. S. G. C.

Microchemical

Microchemical References. 1932. (Part I, Supplement to *Mikrochem.*, 1933, **13**; *ibid.*, 1932. Part II, Supplement to *Mikrochem.*, 1934, **14**; *ibid.*, 1933. Part I, Supplement to *Mikrochem.*, 1934, **15**.)—References collected mainly from abstracts in the *Chem. Zentralblatt*, arranged in the alphabetical order of the authors' names under the following general divisions:—*Pure Microchemistry.*—(i) General and apparatus, (ii) Inorganic analysis, (iii) Organic analysis, (iv) Preparative chemistry, (v) Physical chemistry. *Applied Microchemistry.*—(i) Biology, (ii) Medical and pharmaceutical chemistry, (iii) Mineralogical chemistry, (iv) Technical microchemistry. J. W. M.

Collected References. Spectral Analysis. F. Pavelka and H. Molterer. (*Mikrochem.*, 1935, **17**, 47–102.)—An account of the qualitative and quantitative methods and the apparatus used, followed by 125 references with brief abstracts of each, and 5 tables consisting of photographs of spectra. J. W. M.

Collected References. Carbohydrates, II. A. Wasitzky. (*Mikrochem.*, 1934–35, **16**, 87–114.)—The references collected include qualitative micro-reactions of carbohydrates and their analytical application, especially in the food industries; the use of quantitative micro-methods in biology and in the food industries and food inspection, and the progress of microchemical carbohydrate analysis in general, 1931–34. A number of tests and methods are described with working details, and, in all, 114 references are given. J. W. M.

Spot Tests for Organic Compounds. V. F. Feigl, V. Anger and R. Zappert. (*Mikrochem.*, 1934, **15**, 190–195.)—(i) *Test for hydrazine derivatives.*—Many azo-dyestuffs formed by the coupling of diazotised *p*-amino-benzaldehyde with naphthol- and amino-naphthol-sulphonic acids form with organic hydrazine derivatives hydrazones which may possess an appreciably deeper colour than the original dyestuff. Of a large number of dyestuffs tried, the following were found to be most useful as reagents for hydrazine derivatives. (i) The azo dye formed from diazotised *p*-amino-benzyaldehyde and crocein acid (2-naphthol-8-sulphonic acid) (yellow). (ii) The azo dye formed from diazotised *p*-amino-benzaldehyde and Schäffer's acid (2-naphthol-6-sulphonic acid) (orange-yellow). (iii) The azo dye from diazotised *p*-amino-benzaldehyde and R-acid (2-naphthol-3,6-disulphonic acid) (orange). (iv) The azo dye from diazotised *p*-amino-benzaldehyde and nigrotinic acid (2,8-dihydroxynaphthalene-6-sulpho-4-carboxylic acid) (bright cherry-red). The colours refer to those of the very dilute weak acetic acid solutions. These dyestuffs have not yet been isolated as the pure solids. *Method.*—A drop of the dilute acetic acid solution of the dyestuff is mixed with a drop of a 10 per cent. solution of sodium acetate in a micro-crucible, and a drop of the aqueous or alcoholic solution of the test solution is added. The time for the colour-change depends on the concentration of the test solution, and may be as long as 15 minutes, in which case a blank test is recommended. *Preparation of the reagent.*—*p*-Amino-benzaldehyde hydrochloride is suspended in dilute hydrochloric acid, and diazotised with the calculated amount of sodium nitrite. The diazonium salt solution is poured into the solution (containing excess of soda) of the equivalent amount of the naphtholsulphonic acid, and finally acidified with acetic acid; the solution of the dyes will keep. A table is given showing the reactions of 13 different hydrazines with the 4 different reagents, together with the colour-change and the identification-limit in each case; the identification-limit varies from 50γ to 1γ.

2. *Test for aromatic and α-β-unsaturated aldehydes.*—Sodium pentacyano-amino-ferroate has been found (*Mikrochem.*, 1934, **15**, 183, Abst., ANALYST, 1935, 123) to give an intense blue colour with certain thio-ketones and with aromatic and α-β-unsaturated aldehydes, in the presence of hydrogen sulphide:

$$R.\mathrm{CHO} + \mathrm{H_2S} = R.\mathrm{CHS} + \mathrm{H_2O}$$

$$\mathrm{Na_3[Fe(CN)_5NH_3]} + R.\mathrm{CHS} = \mathrm{Na_3[Fe(CN)_5(}R.\mathrm{CHS)]} + \mathrm{NH_3}.$$

This reaction has been adopted as a micro-test. *Method.*—A drop of the 1 per cent. solution of the reagent is mixed with a drop of a 2 per cent. solution of ammonium sulphide, free from polysulphides, in a micro-crucible and a drop of the aqueous or alcoholic test solution, together with $N/2$ acetic acid solution, is added. An intense blue colour (green in a few cases) results. A blank test should be carried out, and the acetic acid solution should not be too strong. A table is given of the sensitivity of the test and the colours formed with 15 aldehydes. The identification-limit varies from 1γ to 4γ.

J. W. M.

Micro-determination of Bromides and Iodides in Presence of Chlorides. I. Bellucci. (*Gazz. Chim. Ital.*, 1934, **64**, 688–695.)—The ash obtained from blood in the way described (*cf.* Abst., p. 264) contains the whole of the chlorine, bromine and iodine of the original blood in the form of sodium halide salts. When the ash is extracted with 95 per cent. alcohol, a little of the sodium chloride and the whole of the sodium bromide and iodide are dissolved. Evaporation of the alcoholic extract to dryness and solution of the residue in water yields a solution (10 to 15 ml.) in which the bromine and iodine ions may be determined as follows:—The solution is acidified with sulphuric acid and then treated with a slight excess of sodium nitrite, the nitrous acid thus formed liberating the iodine from the iodide, with formation of nitric oxide, whilst the hydrochloric and hydrobromic acids remain unchanged. The free iodine is removed from the aqueous solution by means of carbon tetrachloride, which is then separated, treated, drop by drop, with sodium hydroxide solution (1 : 10) until decolorised, and evaporated to dryness. The residue is dissolved in water and the sodium iodide present in the solution is oxidised to iodate by permanganate and alkali hydroxide. Excess of permanganate is destroyed and, after removal of manganese dioxide, any nitrite present is decomposed by urea after addition of acetic acid. The iodine is then determined as already described (*loc. cit.*). The aqueous solution, containing all the bromide and part of the chloride, is made faintly alkaline with sodium hydroxide and evaporated to dryness on a water-bath. The residue is extracted at the ordinary temperature with acetone, which dissolves the sodium bromide, but not the sodium chloride. The acetone extract is filtered and titrated directly with 0·01 *N* silver nitrate solution in presence of ferric alum. Determinations of bromine and iodine ions in this way in test solutions containing small proportions of sodium chloride, bromide and iodide show the method to be accurate.

T. H. P.

Physical Methods, Apparatus, etc.

Determination of Free Silica. H. L. Ross and F. W. Sehl. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 30–32.)—A petrographic immersion method is described for the determination of free silica in mineral and dust samples. It depends on counting under the microscope the number of transparent particles visible when a definite amount of the material is suspended (*a*) in fennel-seed oil, which has a slightly lower *n* than quartz, (*b*) in nitrobenzene, which has a slightly higher *n* than quartz. The numerical difference between the counts gives a measure of the proportion of particles of quartz or free silica present. To obtain the proportion by weight of quartz particles, account has to be taken of the relative sizes of the particles, which may be measured microscopically. For details of the method, with a description of the optical equipment necessary, the original paper should be consulted.

S. G. C.

Measurement of the Colour of Liquids. Application to Wines. A. Faure and R. Pallu. (*Ann. Falsif.*, 1935, 28, 5–9.)—If a monochromatic ray of light of intensity I_0 falls on a cell with parallel faces containing the wine, then the optical density (D) = log I_0/I_1, where I_1 is the intensity of the transmitted ray. D is a function of the "sale value of the colour" of the wine, the unit of colour-intensity of a wine being known as the "ROB" where 1 ROB = constant × D; a photocolorimeter may then be calibrated in terms of the ROB, on the assumptions that the walls of the cell and the water used for dilution have an optical density of zero, and that the process of dilution involves no physical or chemical change in the colouring matter. It is shown theoretically that these assumptions are justified. White light is unsuitable, because the transmission spectrum contains a pronounced red ray (at 600 to 700$m\mu$), which is independent of the colour of the wine, but blue light (460$m\mu$) gives a ray which corresponds with variations in the colour of the wine as observed by the human eye. A Toussaint photo-electric colorimeter was used, the light being passed through a blue glass filter and a cell 5 mm. thick containing the wine before falling on the potassium photo-electric cell. The resulting current is amplified and measured on a milliammeter, the cell being first calibrated by observing the currents produced after dilution of a strongly coloured wine to various extents; the undiluted wine was given a value of 100 ROB units. It is also desirable occasionally to test the apparatus with various thicknesses of a standard solution of gentian violet (which is stored in the dark), so as to ensure that the cell and its amplifier are giving regular responses. The method gives reliable results, and is more sensitive than the human eye. Table wines have values of 50 to 115, red wines about 15, and coloured wines 600 to 700 ROBS; it is possible to predetermine the final colour of a wine from the value at the time of clearing, so long as no precipitation of colouring matter occurs. J. G.

Reviews

ELEMENTARY ANALYTICAL CHEMISTRY: QUALITATIVE AND QUANTITATIVE (CLOWES AND COLEMAN). Twelfth Edition. Revised by C. G. LYONS, M.A., Ph.D., and F. N. APPLEYARD, B.Sc., F.I.C., Ph.C. Pp. xiii+242. London: J. & A. Churchill, Ltd. 1934. Price 6s.

For the twelfth edition, this well-known text-book has been revised and partly re-written in order to bring into it such modern developments of analytical chemistry as can be advantageously introduced into elementary work. The text is arranged in five main divisions, *viz.* qualitative inorganic analysis, volumetric analysis, gravimetric analysis, inorganic preparations and organic compounds.

The qualitative section, which is on orthodox lines, is exceptionally full and clear. The introduction of the use of α-nitroso-β-naphthol and dimethyl glyoxime as confirmatory tests for cobalt and nickel, respectively, strikes a more modern note. In the 134 pages devoted to this section only one trifling misstatement has been found—the existence of a precipitant for nitrates is denied, nitron being overlooked.

The section on volumetric analysis has been entirely re-written, and is now very comprehensive. It is a pity, however, that, although a method resembling that of the N.P.L. for standardising a burette is given, no mention is made of the procedure for a pipette, and the student is still left to struggle with the problem of the "last drop." The subsections on indicators and hydrogen ion concentration are brief but adequate, although perhaps the distinction between ionised and ionisable hydrogen might have been more strongly emphasised. Many modifications are introduced, such as, for example, the use of diphenylamine as an internal indicator in dichromate titrations. In the organic section are given the reactions of a large number of compounds, including oxalic acid, chloroform, glycine, sucrose, strychnine, and others mainly of pharmaceutical interest.

The new edition is an admirable little volume which provides the student with a firm groundwork of practical chemistry, and neither the authors nor the publishers need fear for the future of "Clowes and Coleman."

HAROLD TOMS

METHODS OF AIR ANALYSIS. By J. S. HALDANE, C.H., M.D., Sc.D., F.R.S., and J. IVON GRAHAM, M.A., M.Sc., F.I.C., F.R.C.Sc.I. Fourth Edition, revised throughout and enlarged. Pp. vii+176, 34 illustrations. London: Charles Griffin & Co., Ltd. Price 7s. 6d.

For many years Dr. Haldane's *Methods of Air Analysis* has been recognised as a work of very great value as a detailed manual of methods which had been abundantly tested by one of the world's leading authorities. The book has now been re-issued, this time with the collaboration of Mr. Ivon Graham, who has added sections which have increased the length by some fifty pages. As was pointed out in previous editions, the book in no way aims at being a treatise on gas analysis, but seeks merely to describe some methods which have been proved reliable. This treatment allows space for very full details of such selected methods.

Apart from the fact that the chapters are now numbered, there is very little alteration in the general appearance of the book. Chapter I contains a new illustrative diagram of the Haldane laboratory gas analysis apparatus; Chapter II is little altered, but has an additional section of 6 pages on an interesting apparatus for the analysis of air samples containing small proportions of higher hydrocarbons, as well as hydrogen, carbon monoxide and methane. Carbon monoxide is determined by oxidation with iodine pentoxide and measurement of the resulting carbon dioxide. In connection with the same apparatus, the authors find that palladium-asbestos at 100° C. satisfactorily effects the selective combustion of hydrogen, saturated hydrocarbons and even carbon monoxide being unaffected. The analyst will be well advised to follow scrupulously the conditions described, since it is known that workers using palladium as an agent for fractional combustion under slightly differing conditions have obtained discordant results.

Chapter III (Calculation and Statement of Results of Analysis) and Chapter IV (Portable Apparatus for Determining small Percentages of Carbon Dioxide) are practically unchanged. The old chapter on portable apparatus for the determination of carbon dioxide, methane and carbon monoxide in mines worked with naked lights is omitted. The chapter on portable apparatus for firedamp determinations is completely rewritten, the McLuckie Gas Detector being described in place of the former apparatus, which was merely a modification of the ordinary Haldane apparatus. Chapter VI, on the approximate determination of oxygen by the flame-test, contains an additional page on the Briggs Safety Lamp. Chapter IX (Determination of Moisture by Dry and Wet-bulb Thermometers) is extended from 3 to 7 pages, and two illustrations are now given. The Storrow and the Hancock types of hygrometer are described, and also the Kata Thermometer. This last instrument is designed to measure the "cooling power" of the atmosphere, which is affected by humidity and the rate of air-circulation, and gives a much better indication of the effect of cold or hot atmospheres on the human body than temperature alone.

Chapter X, which deals mainly with the blood-test for carbon monoxide, contains additional paragraphs on the reaction between haemoglobin and nitric oxide, and on the Hartridge Reversion Spectroscope. One feels that a few more details of this very important instrument might have been given, or, at least, references to books or papers* in which its analytical uses have been described.

Chapter XI, on the accurate determination of very small quantities of carbon monoxide, is entirely new, and was certainly required. The iodine pentoxide method, to which Mr. Graham has made important contributions, is employed; the measure of the carbon monoxide is the iodine liberated, which is determined by titration. Portable and laboratory instruments for this purpose are described and illustrated. The imperative necessity for satisfactory iodine pentoxide is rightly stressed, and details of its preparation given. Chapter XII is a new chapter of 8½ pages on the application of gas analysis to the detection of spontaneous combustion in coal mines. This phenomenon, which has generally been first detected by the smell, can be detected more sensitively (and therefore earlier) by gas analysis. Apparatus for this purpose is described, the gases determined being carbon dioxide and monoxide, the former by absorption and volume-measurement (stated to be accurate to 0·003 per cent.) and the latter by iodine pentoxide and titration of the iodine.

Chapter XIII describes methods for the detection and recording of carbon monoxide. "Hoolamite," which is mentioned but not strongly recommended, is described as iodine pentoxide soaked in sulphuric acid; the mixture devised by Hoover and Lamb and called by this portmanteau name, consists, however, of pumice, iodine pentoxide and *fuming* sulphuric acid. Five very interesting pages are given to the Katz Recorder, in which the carbon monoxide is oxidised by "Hopcalite" catalyst and the heat so produced is recorded by thermo-couples.

Chapter XIV, on the recognition of other poisonous gases, has most usefully been extended from 1½ to 12 pages. A brief synopsis of the toxic properties of a number of gases is given, including, in most cases, an outlined description of a method of detection or determination. In the procedure given for the detection of hydrogen cyanide and cyanogen by the Prussian-blue method, the tyro may be misled by "sulphate" being misprinted as "sulphide." It might have been mentioned that the sensitiveness of the test is greatly increased by filtering after the treatment with ferrous hydroxide, the masking effect of the excess of iron salts being thus greatly reduced. For the same reason the quantity of ferric chloride added after acidification should be very small; "ferric chloride is then added in excess" is, although correct, rather misleading, since, for the quantities of cyanide which are likely to be present, a very small amount of ferric chloride furnishes this necessary excess. On p. 146 occurs the phrase "nitric oxide or nitrogen dioxide, NO (or N_2O_2)." The latter formula—N_2O_2 is, of course, unknown

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* *e.g.* R. C. Frederick, ANALYST, 1931, **56**, 561.

—is made conspicuous by the footnote: "The compounds NO_2 and N_2O_4 have for many years been incorrectly called nitrogen dioxide." Is there, however, any more suitable name available for NO_2 than "nitrogen dioxide," and can it be strictly correct, by whatever authorities it is sanctioned, to apply this name to a molecule (NO) containing only one oxygen atom? The chapter concludes with 4½ valuable pages of tables on the physiological effects of lack of oxygen and of the presence of various proportions of other gases.

Chapter XV, on the determination of dust in air, has been extended from 4 to 15 pages by the addition of a full description of a method of collecting dust for analysis, and an account of those interesting instruments, the Konimeter and the Owens Dust Collector. The book closes with 5 pages of tables of oxygen concentrations corresponding to various proportions of nitrogen, in the ratio existing in fresh air.

It is a tribute to the high excellence of Dr. Haldane's established methods that their description has needed so little alteration. The additions are in all respects cogent, and no greater recommendation could be given than to say that this classic monograph has been worthily brought up to date. H. R. AMBLER

PRACTICAL BACTERIOLOGY FOR STUDENTS OF AGRICULTURE. Second Edition. By ANDREW CUNNINGHAM, D.Sc. Pp. 203. London: Oliver & Boyd. 1934. Price 7s. 6d.

The introductory chapter of this work contains information on general bacteriological technique and deals with a variety of subjects, from the cleaning of glass apparatus to the preparation of culture media.

The author has felt that very elementary advice is worthy of inclusion in a book, and he therefore states, for instance, that a brush should be used in the washing of dirty test tubes, and he includes similar instructions elsewhere. However, every chapter tends to incorporate elementary instruction with advanced practical exercises. Further chapters deal with details of cultural methods and with the diagnosis and characteristics of many organisms, the latter including those found in the soil and in agricultural products, as well as those pathogenic to fowls and other animals.

As the information is almost exclusively of a practical nature, the student should use the book only in conjunction with a treatise on agricultural bacteriology. Then, for example, the association of the subject with the surmises of Pasteur and their exemplification by Warrington, Winogradsky, and others will be appreciated and interest added to the study.

Merely to scan the pages would serve as a reminder of the great extension of the science of bacteriology to many branches of agriculture and its associated industries.

The present volume is the second edition, and any faults that may have been contained in the former now appear to have been corrected. The book is one which can be confidently recommended to practical students, for, in addition to a description of the preparation of culture media and of processes employed in agricultural bacteriology, soil organisms and many others are described.

F. W. F. ARNAUD

A HISTORY OF FOOD ADULTERATION AND ANALYSIS. F. A. FILBY, M.Sc., Ph.D. Pp. 269. London: Allen & Unwin. 1934. Price 10s.

This volume is one of much interest to public analysts and all others interested in the chemistry of food. It is a thesis approved for the degree of Doctor of Philosophy in the University of London, and is graced most appropriately by a foreword by Dr. Bernard Dyer.

It is evidently the result of much patient research, often in recondite directions, and supplies information not readily available in any other treatise—not even in the admirable summary by Wynter Blyth with which all of us are familiar. Dr. Filby takes up the narrative with the beginnings of the ancient city companies which are traced from the Pepperers of Ethelred's days who first formed the Grocers' Company, and he follows the course of food analysis up to the early days of our own Society and THE ANALYST. The activities, legal and illegal, of the grocers, bakers, brewers, vintners, and distillers are discussed in order, and the nature and extent of adulteration which they practised receive critical survey. In general, it seems probable that the majority were more honest than some authors have suggested, if only for the reason that some of the alleged adulterations would not pay.

The Adam and Eve of public analysts appear to be represented by the Polliciers and Garbelers, whose duties so far back as 1300 included the removal of impurities from spices. But the first person who might really be regarded as the forerunner of the public analyst is Henry Jackson, who, in 1758, personally analysed over 100 different bakers' breads in order to ascertain the true facts in relation to their alleged adulteration. It is interesting to note how stoutly the author defends the bakers against the extravagant charges which, ever since the days of Pharaoh, have been so often made against them. He shows very reasonably how absurd are many of the statements originating in the alarmist anonymous treatise of 1757 and repeated in many subsequent works for a century. The humorous story of the baker's reply is well told.

It is not possible in this brief review to refer to the many interesting matters mentioned, though it may be noted, in passing, how history repeats itself—there is nothing new under the sun. Boerhaave, in 1735, gave a reliable test for copper in pickles and the like, and in 1755 there was published a tract, "Serious Reflections on the Dangers attending the use of Copper Vessels." Have we not, in 1935, had examples of this danger in tomato purée and other products?

We are glad to note that Dr. Filby pays tribute to the influence of food adulteration and the early analysts upon the development of the science of chemistry. The volume is a scholarly little treatise, well documented, free from sensationalism or exaggeration; one which we cordially welcome.

H. E. COX

Publications Received

INDIVIDUAL HEALTH. By E. OBERMER. Vol. I. BIOCHEMICAL TECHNIQUE (by E. OBERMER and R. MILTON). Pp. xvi+244. London: Chapman & Hall. Price 15s. net.

SHELLAC: ITS PRODUCTION, MANUFACTURE, CHEMISTRY, ANALYSIS, COMMERCE AND USES. By E. J. PARRY. Pp. xi+240. London: Pitman. Price 12s. 6d. net.

LAC AND THE INDIAN LAC RESEARCH INSTITUTE. By D. NORRIS, P. M. GLOVER and R. W. ALDIS. Indian Lac Research Institute, Nankam, Bihar and Orissa. Price Rs.2/8.

A SCHEME FOR THE DETECTION OF THE MORE COMMON CLASSES OF CARBON COMPOUNDS. By F. E. WESTON. Sixth Edition. London: Longmans, Green & Co. Price 4s. 6d.

THE NATURAL LOGARITHM. By SIR CHARLES VERNON BOYS. Pp. 31. London: Wightman & Co. Price 2s.

TABLE OF INCOMPATIBLES. By W. R. WORRALL. London: John Bale, Sons & Danielson. Price 1s. 6d.

FOURTH PUBLIC HEALTH CONGRESS AND EXHIBITION, 1934. FINAL REPORT. Pp. 477. London: The Congress Organising Council.

A GERMAN-ENGLISH DICTIONARY FOR CHEMISTS. By A. M. PATTERSON. Second Edition. London: Chapman & Hall. Price 15s. net.

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 3rd, Mr. John Evans, President, being in the chair.

Certificates were read in favour of:—William Godden, B.Sc., F.I.C., and Frank Morton, B.Sc., A.I.C.

The following were elected members of the Society:—Frank Bell, Ph.D., D.Sc., F.I.C., James Talmage Dobbins, A.M., Ph.D., Daniel Joseph O'Sullivan, M.Sc., F.I.C.

The following papers were read and discussed:—"Commercial Ground Almonds and their Adulteration," by G. N. Grinling, F.I.C.; "The Detection of Japanese Mint Oil in Peppermint Oils," by D. C. Garratt, B.Sc., Ph.D., F.I.C.; "Measurement of the Small Volumes of Nitrogen obtained by the Micro-Dumas Method," by H. C. Gull, M.Sc.; and "The Application of Analysis to the Study of Liesegang Rings," by E. B. Hughes, M.Sc., F.I.C.

NORTH OF ENGLAND SECTION

On the invitation of Mr. Arnold R. Tankard, F.I.C., a meeting of the Section was held at Hull on April 6th, 1935. There was an attendance of thirty-seven; the Chairman (Professor W. H. Roberts) presided.

After a short address, given by Mr. Tankard, the members inspected the new analytical and bacteriological laboratories of the City of Hull.

Deaths

With deep regret we record the following deaths:—

Leonard Archbutt (Past-President),
Charles Frederick Cross,
Arthur John Starey.

Obituary notices will be published later.

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXVIII. The Separation of the Rare Earths from the Earth Acids

BY W. R. SCHOELLER, PH.D., F.I.C., AND E. F. WATERHOUSE

(*Work done under the Society's Analytical Investigation Scheme*)

FROM the point of view of their rare-earth (*i.e.* yttria- and ceria-earth) content, earth-acid minerals may be subdivided into two groups: (1) Those containing rare earths as essential or major constituents; and (2) those in which the rare earths occur in subordinate down to minute quantities. The analysis of minerals of the first group is discussed in Part I of this section; the determination of the small amounts of rare earths in minerals of the second group forms the subject of Part II.

The pure preparations of ceria, lanthana, neodymia, and thoria used in this research were kindly placed at our disposal by Messrs. Thorium, Limited, through their works manager, Mr. H. F. V. Little, who was also good enough to criticise the manuscript of this paper.

PART I. MINERALS RICH IN RARE EARTHS

The better-known of these exceedingly complex minerals are fergusonite, samarskite, yttrotantalite, euxenite, and aeschynite. It may be noted that the ceria earths preponderate over the yttria earths in aeschynite, the reverse being the case in the other four species.

The analysis of minerals of this class has been greatly facilitated by the labours of J. Lawrence Smith, to whom we owe the process based on decomposition of the mineral by hydrofluoric acid.[1] The earth acids (and titania, zirconia, and tungstic acid) thus go into solution, whilst the rare earths and thoria are converted into insoluble fluorides. Hillebrand and Lundell[2] describe the method and comment upon it in the following terms: "When applicable it should always be used, for it affords very quickly and easily an almost perfect separation of the insoluble rare-earth and alkaline-earth fluorides from the soluble fluorides of the earth-acid and other metals. The method introduces no alkali salts, and has the further advantage, shared by no other, not only of showing whether quadrivalent uranium is present, but also of separating it from sexivalent uranium if both are present."

Smith's process has been studied by Hillebrand[3] and by Wells.[4] The latter's paper is particularly valuable, as it shows the quantitative distribution of the mineral constituents between the fluoride solution and the insoluble fluoride fraction in a samarskite analysis, Wells observing that the method "is not as simple or clean-cut in its separations as the original description might lead one to suppose." However, the summation of his results shows that the earth acids and titania (as well as the small amounts of tin, tungsten, and zirconium present) are found wholly in the fluoride solution, whilst the insoluble fraction contains the whole of the rare earths and thoria. Uranium, being present in the uranous, as well as the uranic, condition, figures in both fractions. The eight remaining constituents, shown by Wells to distribute themselves between the two fractions, are all common elements. We may sum up his experimental evidence by saying that a quantitative separation of the rare earths and thoria from the earth acids, titanium, tungsten, etc., is achieved, but that a number of common elements will be found in the solution as well as in the precipitate. Their distribution between the two fractions is a minor disadvantage of this valuable process, as the two fractions, after the recovery of the rarer elements contained therein, may be combined for the determination of the common metals.

In Smith's process the insoluble rare-earth fluorides are filtered off and converted into sulphates for analysis by the usual methods. The fluoride filtrate also is evaporated with sulphuric acid until the whole of the hydrofluoric acid is expelled; the acid is diluted with water, and the liquid boiled for the hydrolytic precipitation of the earth acids. Instead of using that time-honoured procedure, the disadvantages of which we have discussed in Section XII,[5] we dissolve the acid residue in tartaric acid (with or without previous conversion into a bisulphate melt), according to the general plan laid down in Section I.[6] This course is recommended also by Hillebrand and Lundell.[2] We are now endeavouring to effect the quantitative recovery of the small amounts of tungsten, generally present in the minerals under discussion, from the tartrate solution containing substantial quantities of earth acids with titania and zirconia. The investigation will, we hope, form the subject of a separate Section.

Our experimental work, described in Part II below, has convinced us that the direct application of Schoeller and Powell's scheme of bisulphate fusion and tartaric-acid leaching to minerals containing the earth acids and rare earths as chief constituents, would be inconvenient and even undesirable. Inconvenient, because the solution of the bisulphate melt in tartaric acid would be complicated by the formation of sparingly soluble, double rare-earth sulphates; and undesirable, because the recovery of large amounts of rare earths from tartrate solutions containing earth acid, titania, etc., is less accurate, at any rate, than the fluoride method. We are satisfied that J. L. Smith's process, whilst doubtless requiring further study, is by far the best procedure for the analysis of the minerals here discussed.

PART II. MINERALS POOR IN RARE EARTHS

The principal object of this investigation was to study the analytical problem of the recovery of small quantities of rare earths from tartrate solutions containing earth acids, since fusion with bisulphate and lixiviation with tartaric acid form the starting-point of our scheme outlined in Section I.[6] Before discussing that work we will briefly describe our investigation of a procedure suggested by Pied[7] for the isolation of the rare earths and thoria from earth-acid minerals.

A. PIED'S PROPOSED PROCEDURE.—Pied's paper deals with the precipitation of the earth acids by cupferron[8] from oxalo-tartaric solution after the removal of iron as sulphide. The paper concludes with a seven-line paragraph containing the following passage in literal translation: "I have ascertained that the oxalic solution [of the earth acids] can be obtained by direct treatment of the fused mass obtained from the calcined oxides and many minerals by an attack with pyrosulphate. The rare earths and thorium do not hinder the dissolution; they form a crystalline precipitate, the size of which allows of their evaluation (*dont l'importance permet d'évaluer leur teneur*) in the mineral."

We are not sure whether the quotation from the French text is to be interpreted in a quantitative sense, especially as the paper contains no numerical data. However, we considered the proposed procedure sufficiently interesting for a quantitative investigation. A number of tests were conducted with lanthana, ceria, neodymia, yttria, and thoria, with and without earth acids.

The oxides were fused with potassium bisulphate (3 g.), and the fused mass was extracted with 100 ml. of hot oxalic acid solution (2 to 6 per cent.); the liquid was allowed to stand in the cold, either overnight or some days. The precipitate was collected, washed with weak oxalic acid solution, ignited, and weighed. Only the lanthanum oxalate was markedly crystalline; the others were more or less amorphous, and accordingly did not filter well. The test separations of rare earths from the earth acids gave indifferent results. We need not reproduce more than four, in which 2 per cent. oxalic acid solution was used for extracting the bisulphate melt:

Exp.	Taken g.	Added g.	Ignited oxalate ppt. g.
1	La_2O_3 0·0132	Ta_2O_5 0·1542	0·0416, containing Ta_2O_5
2	,, 0·0125	Nb_2O_5 0·1534	0·0113. Error − 0·0012
3	CeO_2 0·0170	Ta_2O_5 0·1550	0·0417, containing Ta_2O_5
4	,, 0·0189	Nb_2O_5 0·1512	0·0184. Error − 0·0005

The tests disclose a marked difference between tantalic and niobic oxides. Whilst the latter was readily soluble in the reagents used, the former contaminated the oxalate residue to such an extent that the ignited precipitate contained more tantalic oxide than rare earth. This is explained by the fact that oxalic acid is a poor solvent for tantalic oxide: Britton and Robinson[9] state that 0·3 g. required a solution containing 9 g. of crystallised oxalic acid. The use of larger volumes of solvent would be attended with an increased negative error, caused by the slight but appreciable solubility of the rare-earth oxalates. We tried application of 6 per cent. oxalic acid, but experienced trouble in the deposition overnight of coarse crystals of potassium quadroxalate. We tentatively applied leaching of the bisulphate melt with ammonium oxalate solution which, though a more efficient solvent for tantalic-oxide melts, has the disadvantage of dissolving perceptible quantities of the oxalates of the yttrium group; and, whilst it dissolves thorium oxalate, it does not bring about a complete separation of thoria from the rare earths. Of three tests with tantalum and cerium, two gave oxalate precipitates contaminated with tantalum; one gave a correct result. Two tests with tantalum and lanthanum proved a failure: the precipitate slimed badly in one test, and in the other the lanthana recovery showed a large negative error.

We came to the conclusion that the method proposed by Pied is not suitable for quantitative separations of amounts exceeding a few centigrams. In Exps. 14 to 20, described below, the procedure worked satisfactorily with the small quantities involved.

REACTIONS OF THE RARE EARTHS IN TARTRATE SOLUTION

These will be considered under three heads: (B) Precipitation of the Oxalates. (C) Action of Tannin. (D) Behaviour in Tartaric Hydrolysis.

B. PRECIPITATION OF THE OXALATES.—This work was undertaken with a view to recovering subordinate amounts of rare earths, by means of oxalic acid, from the tartrate solution of a bisulphate melt containing earth acid.

The mixed oxides (0·15 g. of pentoxide and 0·015 g. of rare earth) were fused with bisulphate (3 g.), the melt was dissolved in 50 ml. of hot tartaric acid solution (6 to 8 per cent.), and the liquid (100 ml.) was treated with 10 ml. of saturated oxalic acid solution. After standing overnight, or for some days, the precipitate was collected, washed with dilute oxalic acid solution, and ignited to oxide.

It was found that, when much tantalum is present, the addition of oxalic acid to the tartrate solution causes gradual flocculation of tantalic acid. Digestion of the washed precipitate with fresh oxalic acid removes the tantalic acid, leaving the rare-earth oxalate. Such a procedure is again open to the objection that it may increase the slight solubility loss of rare earth; hence we do not consider it suitable for recovering small quantities of rare earths from tartrate solutions containing much earth acid. On the other hand, we have found it useful for quantities not exceeding a few cg., and have applied it in our separation method described below (under D, Exps. 21 to 28).

C. ACTION OF TANNIN.—The improvements achieved in the analytical chemistry of the earth acids and a number of other earths by the agency of tannin[10] induced us to investigate the possibilities of this reagent in the analysis of the rare earths; so far as we know, the subject had never before been studied.

We ascertained that tannin complexes of the rare earths are precipitated from their solutions on addition of tannin and an excess of ammonia. The precipitation takes place in tartrate solutions also. The precipitates are colourless, excess of tannin causing a pale-brown discoloration, as in the case of alumina; the cerium precipitate, however, darkens considerably on exposure to the air; it often turns almost black on the filter. Unlike the aluminium precipitate, the rare-earth complexes are readily soluble upon acidification with acetic acid of the liquid in which they are suspended; in this respect they behave like the precipitates of beryllium and manganese.[11]

For the quantitative investigation of the reaction we prepared solutions containing known amounts of cerium and of yttrium. Measured portions were diluted to 200 ml., boiled, and treated with the following reagents:—25 ml. of saturated ammonium chloride solution, 5 g. of sodium acetate, 0·5 g. of tannin in freshly-prepared solution, and ammonia (1 : 3) until its smell became pronounced. In the tartrate tests, tartaric acid (4 g.) was added before the ammonia. The precipitates were allowed to settle on the water-bath, collected, well washed with ammonium nitrate solution, ignited strongly, and weighed:

Exp.	Taken g.	Solution	Found g.	Error
5	CeO_2 0·0500	Acetate	0·0500	0·0000
6	,, 0·0500	Tartrate	0·0496	−0·0004
7	Y_2O_3 0·0508	Acetate	0·0522	+0·0014
8	,, 0·0508	Tartrate	0·0508	0·0000

Having demonstrated the quantitative recovery of the two earths from ammoniacal tartrate solution, as well as the ready solubility of their tannin complexes in dilute acetic acid, we proceeded to investigate the separation of small quantities of rare earths from the earth acids. The latter, it will be recalled, are quantitatively precipitated from feebly-acid tartrate solutions containing acetate.[8]

We conducted 9 experiments on mixtures of pentoxide and ceria. Tantalic oxide was taken in 5, niobic in 4, tests. It was found that partial co-precipitation of ceria (shown by the excessive weight and the yellow to buff colour of the ignited tannin precipitate, *TP*) took place under the conditions given in Section XVII[8] for the complete precipitation of the earth acids (Exp. 9, below). In a tantalum solution containing 5 ml. of acetic acid in 100 ml. total bulk, tannin produced no precipitate; subsequent neutralisation with ammonia until the pure yellow colour of the tantalum precipitate showed signs of bleaching (co-precipitation of traces of iron at the neutral point) gave a seemingly good separation (Exp. 10). These conditions and results could not be reproduced with niobium. In Exps. 11 and 12, the earth acid was precipitated from the tartrate solution half-saturated with ammonium chloride after neutralisation of the tartaric acid with ammonia, the resultant acidity of the solution being that of the pyrosulphate after fusion.

Exp.	Taken M_2O_5 g.	 CeO_2 g.	Tannin added g.	Saturated NH_4Cl sol. in 250 ml.	*TP* g.
9	Ta_2O_5 0·1510	0·0235	1	30 ml.	0·1676
10	,, 0·2042	0·0240	1·2	25 ,,	0·2047
11	,, 0·2020	0·0232	2	equal bulk	0·2020
12	Nb_2O_5 0·2020	0·0234	2	,, ,,	0·1952
13	,, 0·2046	0·0253	2	,, ,,	0·2203

This procedure gave a serviceable tantalum, but low niobium, recovery. In Exp. 13 we precipitated the niobium in half-saturated ammonium chloride solution, but neutralised the solution completely after addition of tannin in the manner described for "Zirconia and Titania."[8] The resultant niobium precipitate was now strongly contaminated with ceria.

We may conclude that the interval between complete tantalum and incipient cerium precipitation appears to be wide enough to render their separation possible. On the other hand, complete precipitation of niobium was not achieved in our experiments without extensive co-precipitation of cerium. We doubt whether tannin could achieve a quantitative separation of the rare earths from the earth acids without recourse to a process of fractional precipitation.

D. BEHAVIOUR IN TARTARIC HYDROLYSIS.—In Section XVI[12] four experiments were made on tartaric hydrolysis of the earth acids in presence of thoria; it was found that the precipitates, *HP*, occluded thoria. In two tests made with "ceria earths of unknown purity," no co-precipitation could be observed. The present sub-section is a continuation of the earlier work, which was suspended for want of pure rare-earth preparations.

Our experiments (19 and 20) confirmed the co-precipitation of thoria. In the final series of tests, reproduced below, we definitely proved the precipitated earth acids to be free from rare earths. The bisulphate melt of the mixed oxides was dissolved in 50 ml. of 8 per cent. tartaric acid solution, the solution (300 ml.) was boiled with 30 ml. of strong hydrochloric acid, the precipitate HP^1 was collected, returned to the beaker, and well churned up with filter-pulp and wash-liquor for the complete removal of any soluble rare-earth salts; the precipitate was then returned to the filter, and the washing concluded as usual. The precipitate was ignited, and submitted to the same sequence of operations. The products were a second precipitate, HP^2 (which was discarded), and the filtrate therefrom, containing any rare earth occluded in HP^1, together with the few mg. of earth acid that normally escape precipitation. The oxides in these filtrates were recovered by precipitation with tannin and excess of ammonia (as under C above), and the small precipitate, TP^2, was ignited and weighed.

The filtrate from HP^1, containing the rare earths and a few mg. of earth acid, was treated with tannin and ammonia exactly as the filtrate from HP^2. This gave a precipitate, TP^1, in which the rare earth was determined by the two methods discussed under A and B above.

(A) *By Pied's procedure, i.e.* ignition, bisulphate fusion, extraction of the melt with 5 per cent. oxalic acid, and filtration after standing overnight (Exps. 14 to 20). The filters containing the insoluble oxalates were treated with nitric and sulphuric acids for the destruction of organic matter; the residual acid was diluted and filtered, the filtrate treated with ammonia, and the precipitate ignited and weighed.

	Taken				Rare earth	
Exp.	M_2O_5 g.	Rare earth g.	TP^1 g.	TP^2 g.	in TP^1 g.	Error g.
14	Ta_2O_5 0·2052	CeO_2 0·0211	0·0251	0·0027	0·0200	−0·0011
15	Nb_2O_5 0·2037	,, 0·0220	0·0366	0·0108	0·0216	−0·0004
16	Ta_2O_5 0·2022	Y_2O_3 0·0234	0·0298	0·0025	0·0225	−0·0009
17	Nb_2O_5 0·2013	,, 0·0217	0·0366	0·0084	0·0220	+0·0003
18	Ta_2O_5 0·2026	Nd_2O_3 0·0207	0·0264	0·0022	0·0212	+0·0005

The small precipitates TP^2 were tested for rare earths by fusion with bisulphate and extraction with oxalic acid on a small scale. Such a procedure constitutes a delicate test, but nevertheless it failed to detect any rare earth in the precipitates. What remained insoluble after the extraction weighed a fraction of a mg. and proved to be silica, the usual impurity in tannin precipitates produced in ammoniacal solutions.

In Exps. 19 and 20 we proved the co-precipitation of thoria in tartaric hydrolysis by using the above procedure.

	Taken					
Exp.	M_2O_5 g.	ThO_2 g.	TP^1 g.	ThO_2 in TP^1 g.	TP^2 g.	ThO_2 in TP^2 g.
19	Ta_2O_5 0·2028	0·0239	0·0261	0·0184	0·0065	0·0034
20	Nb_2O_5 0·2048	0·0223	0·0340	0·0197	0·0131	0·0022

(B) *By oxalate precipitation from tartrate solution, i.e.* ignition, fusion with a minimum of *sodium* bisulphate, solution of melt in tartaric acid and filtration to remove silica; precipitation of hot solution (about 50 ml.) with oxalic acid during agitation; filtration next day, and cautious ignition of oxalate to oxide.

Method B was suggested by Mr. H. F. V. Little as an alternative to A. On the whole, we give preference to Method B; it certainly saves time and labour. We noticed one slight disadvantage, *viz.* that the clear filtrate from the oxalate precipitate, *OP*, on being mingled with the oxalic-acid washings, almost invariably deposited a further small crop of crystals yielding a mg. or less of rare earth; this was collected separately. The figures given under *OP*, Exps. 21 to 28, represent the combined weights of the ignited oxalate precipitates:

	Taken				
Exp.	M_2O_5 g.	Rare earth g.	*TP* g.	*OP* g.	Rare-earth error
21	Ta_2O_5 0·2018	CeO_2 0·0224	0·0274	0·0219	−0·0005
22	Nb_2O_5 0·2010	,, 0·0247	0·0377	0·0252	+0·0005
23	Ta_2O_5 0·2058	,, 0·0251	0·0308	0·0243	−0·0008
24	Nb_2O_5 0·2054	,, 0·0219	0·0404	0·0217	−0·0002
25	Ta_2O_5 0·2020	Y_2O_3 0·0234	0·0300	0·0231	−0·0003
26	Nb_2O_5 0·2022	,, 0·0230	0·0370	0·0235	+0·0005
27	Ta_2O_5 0·2048	Nd_2O_3 0·0284	0·0360	0·0272	−0·0012
28	Nb_2O_5 0·2024	,, 0·0250	0·0394	0·0245	−0·0005

E. ANALYTICAL APPLICATION.—The above combination of procedures, *viz.* (*α*) tartaric hydrolysis (single precipitation), (*β*) tannin precipitation from ammoniacal tartrate solution, and (*γ*) extraction of the bisulphate melt of the ignited tannin precipitate with oxalic acid solution or precipitation of the oxalates from tartrate solution—either procedure on a small scale—forms what we consider the most reliable means for the determination and identification of small quantities of rare earths in earth-acid minerals. Tartaric hydrolysis eliminates the earth acids (all but a few mg.) as a precipitate free from rare earths, the non-precipitated earth acid acting as a collector in the subsequent tannin precipitation if the rare earths are very subordinate.

The new process effects a far better separation than the obsolete pyrosulphate hydrolysis method,[5] in which the insoluble earth-acid residue from the extraction of the bisulphate melt retains appreciable quantities of other earths.

The ignited rare earths should, of course, be tested for thoria. A more complex separation case affecting the rare earths as mineral associates of the earth acids has yet to be investigated, *viz.* the separation of small amounts of rare earths from the pentoxide and dioxide earths.

SUMMARY.—For the separation of large quantities of rare earths from the earth acids, J. L. Smith's hydrofluoric acid method is considered to be the best. The application of our tartaric acid scheme to the soluble fluoride fraction obtained in Smith's method is an improvement on the original procedure.

Certain processes for the separation of small amounts of rare earths from much earth acid were studied. (1) Pied's proposed method (extraction of a bisulphate melt with oxalic acid solution) is not to be recommended except on a centigram scale. (2) The direct precipitation of the oxalates from a tartrate solution containing much earth acid is not suitable for the recovery of the rare earths; on a small scale, however (*i.e.* with 2 cg. or less of pentoxide), the method is quite satisfactory. (3) Tannin quantitatively precipitates the rare earths from ammoniacal tartrate solution; the precipitates are readily soluble in acetic acid. Tannin precipitation from feebly acid tartrate solution does not effect a clean-cut separation of the rare earths from the earth acids. (4) When the earth acids are precipitated by tartaric hydrolysis, the precipitate is quite free from rare earths. (5) We recommend the following separation process: precipitation of the bulk of the earth acids by tartaric hydrolysis, recovery of the rare earths and the balance of the earth acids by tannin precipitation from the ammoniacal filtrate, fusion of the ignited small tannin precipitate with bisulphate, and extraction of the melt with oxalic acid solution, or solution of the melt in tartaric acid and precipitation of the rare earths with oxalic acid.

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A New Volumetric Method for the Determination of Beryllium*

BY B. S. EVANS, M.C., D.Sc., F.I.C.

BERYLLIUM, in spite of its high price, is being increasingly used as a component of certain alloys, notably those containing copper. The process which is the subject of this paper was originally worked out to provide a method for its determination in a series of beryllium-lead alloys; although it was subsequently found that beryllium does not appear to mix with lead, this does not detract from any value the process itself may have.

The process is based primarily on the very low equivalent weight of beryllium (4·51), which causes it to combine with a relatively large amount of acid; hence, if it can be made to act as an alkali which can be titrated with standard acid, the conversion factor, acid consumed: beryllium, is very low, instead of being, as in the case of most metals, unmanageably high; thus:

1 ml. of $N/10$ acid $\equiv$ 0·00045 g. of beryllium
,, ,, ,, $\equiv$ 0·00327 g. of zinc

Added to this are the facts that beryllium salts are, momentarily, not precipitated by an iodide-iodate mixture and that they are soluble in sodium bicarbonate solution, thus rendering possible an iodimetric titration of the excess of acid added.

Details of the process are as follows:—The beryllium, after having been freed from other metals having insoluble hydroxides, is precipitated with ammonia and filtered. The precipitate is dissolved through the filter with 20 ml. of dilute (1 : 1) hydrochloric acid, and the filter is washed with water. About 1 ml. of 0·04 per cent. thymolphthalein solution is added to the filtrate, followed by sodium hydroxide solution until the liquid is dark blue, and then by dilute (1 : 1) hydrochloric acid, drop by drop, until it is again colourless, about 3 drops being added in excess. The solution is now boiled vigorously for ten minutes, after which 2 per cent. solution of sodium hydroxide is added, a few drops at a time, until the liquid becomes a darkish blue, too large an excess being avoided; boiling is then continued for another ten minutes. At the end of this time the blue colour is exactly discharged by titrating the boiling solution with *N*/10 hydrochloric acid; this operation demands care, the colour at the end being faint and only slowly discharged; it is desirable when the colour becomes doubtful to allow the precipitate to settle and to look through the clear liquid at a white tile held diagonally to a window; the first part of the titration should be carried on until the colour is faint and the solution then again heated to boiling before finishing it, drop by drop. A measured excess of *N*/10 hydrochloric acid is next added (the total volume at this point should be at least about 200 ml.; if not, water must be added). The solution is boiled for 1 minute and then cooled; when it is quite cold, 20 ml. of saturated potassium iodate solution are mixed with 20 ml. of 4 per cent. potassium iodide solution and immediately added to it, and the flask is vigorously swirled for 2 or 3 seconds (not longer); about 4 grams of solid sodium bicarbonate are dropped in, the flask is again swirled and the liberated iodine at once titrated with *N*/10 arsenious oxide solution in the ordinary way. The arsenious oxide solution for this titration must not contain free acid; it is made up by dissolving the correct weight of arsenious oxide in sodium hydroxide solution, diluting, acidifying and finally adding an excess of sodium bicarbonate, thoroughly shaking to remove carbon dioxide and diluting to the required volume. The operations from the addition of the iodide-iodate mixture to the end of the titration must be carried through with a minimum of delay. The hydrochloric acid is standardised against the arsenic solution by treating with iodide-iodate mixture and titrating the liberated iodine in the same way. The number of ml. of *N*/10 arsenious oxide solution required for the titration of the sample, deducted from the number required for titrating the measured excess of *N*/10 acid originally added, gives the number of ml. of *N*/10 hydrochloric acid neutralised by the beryllium hydroxide, and this, multiplied by 0·00045, gives the weight in grams of beryllium present.

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* Communication from Research Department, Woolwich.

Experimental determinations of beryllium were carried out by this method, with the following results:

Added g.	$\equiv$ ml. of *N*/10 HCl	Titration (ml. *N*/10 As_2O_3)	Found g.
0·01038	23·05	35·00 − 11·95 = 23·05	0·01038
0·00934	20·75	29·80 − 9·05 = 20·75	0·00934
0·00831	18·45	29·80 − 11·40 = 18·40	0·00828
0·00727	16·15	29·80 − 13·75 = 16·05	0·00722
0·00623	13·85	29·80 − 15·70 = 14·10	0·00635
0·00519	11·55	29·80 − 18·10 = 11·70	0·00526
0·00415	9·22	29·80 − 20·65 = 9·15	0·00412
0·00311	6·91	19·90 − 12·85 = 7·05	0·00317
0·00207	4·60	19·90 − 15·25 = 4·65	0·00209
0·00104	2·31	19·90 − 17·45 = 2·45	0·00110

Separation of beryllium from a large amount of lead was achieved as follows: Quantities of 10 g. each of lead were dissolved in nitric acid, and varying amounts of beryllium were added; 20 ml. of dilute (1 : 3) sulphuric acid were added to each, and the resulting precipitates, after cooling, were filtered off and washed with 2 per cent. sulphuric acid. The filtrates and washings were made alkaline with sodium hydroxide and then neutralised with dilute (1 : 3) sulphuric acid, 2 to 3 ml. excess being added; about 4 g. of sodium bicarbonate were next dropped in cautiously, a little at a time (if a scrap of litmus paper floating in the liquid was not now of a bluish shade more bicarbonate was added), and a rapid stream of hydrogen sulphide was passed for 40 seconds, after which the flasks were left on the steam-bath for about 20 minutes, with occasional agitation. The precipitated lead sulphide was filtered off and washed with hot sodium chloride solution (5 per cent.); the filtrate was made strongly acid with hydrochloric acid and boiled for a few minutes; the sulphur cloud was dispelled by the addition of a solution of bromine in hydrochloric acid, and the excess of bromine was boiled out. After addition of 20 ml. of ammonium chloride solution (20 per cent.) to the filtrate the beryllium was precipitated with ammonia, the liquid was boiled for a minute or two, and the beryllium hydroxide was filtered off and washed with hot ammonium chloride solution (5 per cent.). This precipitate was treated as described in the earlier part of the paper, and the volumetric determination was carried out. The results were as follows:

Lead taken g.	Beryllium added g.	≡ ml. N/10 HCl	Titration (ml. of N/10 As_2O_3)	Beryllium found g.
10·0	0·01038	23·05	29·80 − 6·75 = 23·05	0·01038
10·0	0·00831	18·45	29·80 − 12·00 = 17·80	0·00801
10·0	0·00623	13·85	19·85 − 6·30 = 13·55	0·00610
10·0	0·00415	9·22	19·85 − 10·70 = 9·15	0·00412
10·0	0·00207	4·61	19·85 − 15·05 = 4·80	0·00216

The only part of the volumetric determination which is at all troublesome is the exact neutralisation of the solution with *N*/10 hydrochloric acid, as the colour-change is gradual and very slight; as an offset against this, however, is the very low factor of the beryllium, an error of as much as 1 ml. corresponding to less than 0·5 mg. of beryllium.

Traces of aluminium and iron do not seem to interfere with the titration, but larger amounts must be separated.

The Determination of Traces of Cyanides in Water

By A. E. CHILDS, B.A., B.Sc., and the late W. C. BALL, D.Sc., M.A., F.I.C.

In a recent research[1] into the causes of the high mortality of fish in certain rivers there were early indications that one of the chief factors was the presence, in the water, of cyanides—arising from the discharge of various industrial effluents into the stream. As cyanide compounds are highly toxic to fish—concentrations as low as 0·1 to 0·3 parts per million being poisonous—a method of determining very small quantities of cyanides was essential.

There is a considerable volume of literature on the subject, but, as opinions are somewhat conflicting as to the relative sensitiveness of the various tests, a critical examination was undertaken to determine which of them would be most suitable for the purpose in question.

The tests described in the literature generally give good results with aqueous solutions of pure hydrocyanic acid or readily decomposed cyanides. Many of the tests, however, are not specific, the precipitations or changes in colour upon which they depend being given equally well by other substances, or, in some cases, being inhibited or masked by the presence of impurities.

In testing for cyanides, therefore, in river or other crude waters, it is inadmissible in most cases to apply the tests to the water direct. The impurities must, as far as possible, be removed. This is best achieved by preliminary distillation of the water, the determination of the cyanide being made subsequently on the distillate.

Preliminary Preparation of the Sample.—A known volume of the water to be tested (500 ml. is a convenient quantity) is placed, after filtration from suspended matter, in a round-bottomed flask, fitted with a Liebig condenser. Tartaric acid (0·5 g.) is added to the water, which is then gently distilled, a few fragments of porous pot being added to prevent bumping. Should the sample of water be originally alkaline, it must first be neutralised with tartaric acid, and the 0·5 g. of acid then added.

Hydrocyanic acid is readily volatile in steam and 95 per cent. or more of the cyanides (if readily decomposable) present in the water will be found in the first 25 ml. of the distillate. It is advisable, however, to collect 50 ml. Even then, a small trace of cyanide, which experiment has shown not to exceed 1 per cent. of the amount originally present, still remains in the distillation flask. Should the concentration of cyanide be less than 1 in 10 millions, only 25 ml. of the distillate should be collected. The small loss thus introduced is more than counterbalanced by the greater accuracy obtained in the subsequent determination.

The distillate should be colourless and free from opalescence. If this is not the case, the presence of steam-volatile impurities (*e.g.* phenols, fatty acids, etc.) must be suspected.

As these impurities interfere somewhat with several of the tests described later, it is advisable, if their presence is suspected, to carry out the distillation under reduced pressure and at as low a temperature as practicable. By this means the amount of them found in the distillate will be reduced. It should be borne in mind that, in carrying out this distillation under reduced pressure, a very efficient condenser is required.

Chlorides, bromides, iodides, ferrocyanides, ferricyanides, cyanates, thiocyanates, chromates, and non-volatile substances generally, which may be present in the water under examination, will not be found in the distillate.

If sulphides are present in the water, hydrogen sulphide may be found in the distillate, and will tend to interfere with certain of the tests. If this should be the case, a very slight excess of lead nitrate or acetate solution may be added to the water before the addition of tartaric acid and the lead sulphide produced filtered off before distillation. The addition of the lead salt will cause no loss of cyanide (as lead cyanide) provided that the concentration of cyanide in the water does not exceed 1 part in half a million.

The presence of a sufficiency of a strong oxidising agent in the water may tend to oxidise some of the cyanide to cyanate, which would cause the results obtained from the distillate to be somewhat low.

In the presence of ferrocyanides the results will be high, for distillation of solutions of these compounds with tartaric acid causes the precipitation of ferrous hydrogen ferrocyanide and the liberation of an equivalent quantity of hydrocyanic acid.

After sufficient of the distillate has been collected, it is well mixed and an aliquot part taken for the determination of the hydrocyanic acid therein.

METHOD OF CARRYING OUT THE DETERMINATION

The method recommended is a colorimetric one and depends upon matching the colour produced when known amounts of cyanide are mixed with various reagents, with that produced by a known volume of the distillate—obtained as described above—treated in an identical manner.

For this purpose a series of thin, colourless, flat-bottomed glass tubes, similar to small Nessler glasses is required. These should be as nearly as possible of the same diameter and should be accurately calibrated to 10 ml. (Those used in these experiments were approximately 7·5 cm. long and 1·8 cm. in diameter, and were obtained from Messrs. Baird & Tatlock, Ltd., London.)

Several of these tubes are taken, and a series of standards is made by placing therein known, gradually increasing, amounts of an accurately standardised solution of potassium cyanide. Sufficient distilled water is then added to bring the volume in each to about 8 ml., and a definite volume of the reagent (generally 1 ml.) is added. The contents of the tubes are then accurately made up to 10 ml. with distilled water and throughly mixed.

At the same time a known volume of the distillate, obtained as already described, is treated in an exactly similar manner.

In order to avoid the preparation of a large number of standards, it is advisable to carry out a preliminary test to determine approximately the amount of cyanide present, and then to repeat the test, using a more closely graduated series of standards and bracketing the approximate amount found.

When the colour produced by the test is weak, the matching is best carried out by looking through the depth of the liquid in the tubes, against a white background or, in the case of an opalescence, against a dark background. With the more intense colours (produced by greater amounts of cyanide) an optical arrangement similar to that used in the Lovibond Tintometer will be found to be advantageous, as this apparatus not only evenly illuminates the "standard" and the "unknown" under examination, but also permits of a simultaneous view of both.

ANALYTICAL CONSIDERATION OF THE VARIOUS TESTS.—A critical examination was carried out on upwards of twenty tests (including various modifications thereto) that have from time to time been published. Of these, the following four were found to be the most suitable for the determination of small quantities of cyanides in river or crude waters. Two of them [(*c*) and (*d*)] are not specific for cyanides, but are so much more sensitive than the specific tests (*a*) and (*b*) that, for very low concentrations, the use of one of them is almost obligatory.

(*a*) *Prussian Blue Test.*—This test, which is specific for cyanides (in the absence of ferrocyanides), depends upon the formation of a ferrocyanide when an alkaline solution of an easily decomposable cyanide is warmed with a solution of ferrous sulphate. On subsequent acidification with hydrochloric acid and addition of a small quantity of a ferric salt the deep blue colour of Prussian blue is produced. If, however, a considerable quantity of cyanide is present, the Prussian blue is formed as a dense blue precipitate.

Gentle heat promotes the reaction, but too great an excess of alkali or hydrochloric acid must be avoided.

To carry out the determination of cyanides by this test, the following reagents are required:

An approx. 0·1 per cent. aqueous solution of ferrous sulphate (freshly prepared).
" " 0·1 " " " " " ferric chloride.
" " 1·0 " " " " " sodium hydroxide.
" " 1·0 " " " " " hydrochloric acid.

To a known volume (5 to 8 ml.) of the distillate, obtained as described above, 2 drops of the sodium hydroxide solution are added and then 1 ml. of the ferrous sulphate solution. After gentle warming the mixture is allowed to remain for about 5 minutes, when 5 drops of ferric chloride are added, followed by 1 ml. of 1 per cent. hydrochloric acid. The whole is then made up accurately to 10 ml. with distilled water and well mixed.

The determination of the cyanide is carried out by matching the blue colour produced with that from known amounts of cyanide treated in identical manner.

If a blue precipitate is at once produced, the determination, by colour matching, cannot be accurately carried out, so that, should this occur, a smaller quantity of the solution containing the cyanide must be taken and the test repeated.

Though this test is specific for cyanides and is therefore admirable in that respect, it is not, comparatively speaking, very sensitive. Anderson[2] states that 0·04 mg. of hydrocyanic acid in 10 ml. (1 part in 250,000) can be detected by this test, though in this series of experiments the lowest amount that could be detected was 0·2 mg. in 10 ml. With solutions containing less than 1 part of hydrocyanic acid in 100,000 no reaction was given, irrespective of the volume taken. (This agrees with the later finding of Anderson.[3]) This is probably due to incomplete conversion of the cyanide, at this dilution, into ferrocyanide; since, once Prussian blue has been formed, it can be diluted several times below the concentration limit at which the test, as normally carried out, fails.

The Prussian-blue test, rather than any other, should be used for the determination of cyanides in crude waters, if the concentration therein is not less than 1 part of hydrocyanic acid in 250,000.

(*b*) *Thiocyanate Test.*—This test, in the absence of thiocyanates, is also specific for cyanides. It was found to be about 5 to 10 times as sensitive as the Prussian-blue test.

It is, however, somewhat complicated and tedious to carry out, and at extreme limits of dilution did not prove very reliable. Its use is not recommended.

(*c*) *Silver Cyanide Test.*—This test depends upon the opalescence produced when excess of silver nitrate is added to a slightly acid solution of a cyanide. It is not specific for cyanides, as halogen acids and their salts and certain fatty acids also produce an opalescence with silver nitrate. Sulphides and free hydrogen sulphide interfere by precipitation of the silver.

If the sample of the crude water is subjected to preliminary distillation, no halogen salts or acids can be found in the distillate, unless sufficient oxidising agents are also present to liberate the free halogens. This, however, is extremely unlikely to occur in river water. Stearic acid (and allied compounds) may, however, be found in the distillate and, if present, will interfere with the test by producing an opalescence. Phenolic substances, if present in amounts smaller than that necessary to produce a turbidity in the distillate (before the addition of silver nitrate), do not interfere, though, if this amount is exceeded, they naturally will.

To carry out this test the following reagents are required:—$N/10$ silver nitrate solution; 1 per cent. nitric acid; 1 per cent. ammonia.

To a known volume of the distillate obtained from the water under examination, 5 drops of ammonia and then 3 drops of silver nitrate solution are added. (The presence of the ammonia was found to increase the sensitivity of the test for hydrocyanic acid, though Anderson[3] states the contrary.) This is then acidified with 1 ml. of nitric acid, made up accurately to 10 ml. with distilled water (chloride-free) and well mixed.

The determination of the cyanide present is carried out by matching the opalescence produced with that from known amounts of cyanide.

The limiting concentration at which the opalescence produced by this test can be detected is 0·005 mg. of hydrocyanic acid in 10 ml. of water, *i.e.* 1 part in 2,000,000. With concentrations of 0·02 mg. in 10 ml. (1 part in 500,000) the opalescence is readily distinguishable.

When 500 ml. of the water are distilled in the manner described, this test allows of the detection of 1 part in 5 millions. For concentrations of this order it would appear to be a very reliable method.

(*d*) *Phenolphthalin Test* (Weehuizen's test[4]).—This is a very sensitive test, and, if proper precautions are taken, it can be used for the determination of extremely dilute solutions of cyanides.

It depends for its action on the production of a red colour by the oxidation, in the cold, of an alkaline solution of phenolphthalin to phenolphthalein in the presence of a cyanide and a weak solution of a cupric salt.

It is, however, not specific for cyanides, as other compounds which are able to oxidise the phenolphthalin under these conditions will also give a positive reaction.

To carry out the test, the following reagents are required:—A 0·3 per cent. aqueous solution of copper acetate; 2·5 per cent. aqueous solution of glycerin; 1 per cent. sodium hydroxide solution; and a 1 per cent. aqueous solution of phenolphthalin containing 20 ml. of 1 per cent. sodium hydroxide solution per 100 ml.

It is essential that the phenolphthalin should be of a high order of purity and free from phenolphthalein. That used in these experiments was obtained from The British Drug Houses, Ltd.

To prepare the actual reagent for the test, 10 ml. of the above phenolphthalin solution are diluted to 50 ml. with 2½ per cent. glycerin solution. To this are added 50 ml. of 0·3 per cent. copper acetate solution, and the whole is well mixed, filtered (if cloudy) and kept in a stoppered glass bottle. (The function of the glycerin is to prevent the precipitation of the copper as hydroxide on the subsequent addition to it of caustic soda. It also increases considerably the sensitivity of the test.)

The estimation is carried out by taking a known volume of the solution containing the cyanide and adding to it 1 ml. of the above mixed reagent. Five drops of a 1 per cent. caustic soda solution are then added and the whole is made up accurately to 10 ml. with distilled water and well mixed. The temperature should not be allowed to exceed 15° C.

The amount of cyanide is estimated by matching the reddish colour produced with that obtained from known amounts of cyanide.

Though the colour produced by the test is fairly lasting, it does change with time, so that the matching should be carried out with the minimum of delay.

As mentioned above, the test is not specific for cyanides. Ferricyanides and aqueous solutions of the halogens give a similar coloration. On the other hand, ferrocyanides, chromates, nitric acid, ferric chloride and halogen salts give no reaction, and neither does a weak solution of hydrogen peroxide. One ml. of hydrogen peroxide (20 vols.) diluted to 10 ml. with water does, however, give a slight brownish colour.

Sulphides interfere by precipitating the copper in the reagent, and if present, should be removed from the water before distillation, by the addition of lead nitrate or acetate.

If the sample tested is prepared by distillation of the crude water as described above, no non-volatile impurities will be found in the distillate.

Of the steam-volatile impurities which might be present, fatty acids do not interfere, but phenols, if present in concentration greater than 1 part in 50,000 of the crude water, prevent the full development of depth of colour produced by the cyanide.

The phenolphthalin test gives a faint, but nevertheless perceptible, colour with 0·0005 mg. of hydrocyanic acid in 10 ml. of water (1 part in 20 millions), whilst with 0·002 mg. in the same volume of water the colour produced is quite definite.

Provided that the proper precautions are carried out and that the cyanide present in the crude water is concentrated tenfold by distillation, as described above, this test will give reliable results for the determination of cyanides in concentrations as low as 1 part in 50 millions of the crude water.

The methods recommended for the determination of concentrations of cyanides of the order of one in five millions and lower, are the phenolphthalin and the silver nitrate tests.

With the proper precautions, either of these tests is capable of giving results of a high order of accuracy.

Dr. B. A. Southgate of the Marine Biological Association, who has used these tests in his researches on the estuary waters of the River Tees, has found them reliable and accurate. Duplicate analyses made by him of the cyanide in estuary water taken from the neighbourhood of industrial outfalls gave the following results:

	Cyanogen in g. per 10^6 ml.									
Silver nitrate method	0·55	0·1	0·25	0·65	0·3	0·15	0·05	0·2	0·2	0·4
Phenolphthalin ,,	0·6	0·1	0·2	0·6	0·35	0·1	0·05	0·2	0·3	0·3

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CHEMICAL DEFENCE EXPERIMENTAL STATION
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The Effect of Grinding in a Power Mill on the Albuminoid Content of Feeding Stuffs

BY F. ROBERTSON DODD, F.I.C., AND C. ROBERTSON LOUDEN, B.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, December* 8, 1934)

IN THE ANALYST for September (1934, p. 606) Dr. F. J. Elliott, writing "Notes on the Grinding of Feeding Stuffs in a Power Mill," gives figures relating to decorticated ground-nut cake which purport to show that the preparation of a sample for analysis in such a mill is liable to produce an appreciable loss of albuminoids. Since this is a matter of considerable importance to merchants as well as to analysts, experiments were conducted in our respective laboratories on commercial specimens of feeding stuffs.

The Christie & Norris laboratory mill—which Dr. Elliott described—is in use in both laboratories, but without the balloon attachment. In one case the ground powder is received in a canvas bag tightly sewn on to the sieve; in the other, the box drawer supplied with the machine is used as the receiver.

The 1-mm. sieve prescribed in the Official Regulations was used in each case, and the grinding was continued only until all the sample had passed through the sieve. Three samples were prepared from a ground-nut cake and a cottonseed cake, respectively, one, in each case, being ground by the Christie & Norris machine, one by a cone mill (the Whitmee), and one by mortar and sieve.

The moisture was determined in each sample, with the object of ascertaining whether there were any appreciable differences on this point in the three modes of grinding.

The following are the figures obtained:

Ground-nut cake	Whitmee mill Per Cent.	Christie & Norris mill (with bag receiver) Per Cent.	Mortar and sieve Per Cent.
Loss in weight ..	0·36	1·7	0·56
Moisture	8·45	8·35	8·20
Albuminoids ..	47·38	47·44	47·31
Cottonseed cake			
Loss in weight ..	0·30	1·0	0·30
Moisture	9·25	9·15	9·35
Albuminoids ..	38·69	38·44	38·75

A series of thirty experimental runs conducted by members of the staff on various types of cakes, in the machine fitted with the box receiver, as in everyday practice, *i.e.* without taking any extra precautions to avoid loss of the dust, showed that samples of 100 g. in weight, when passed through the Christie & Norris machine, might lose between 2 and 3 g.

The following figures for albuminoids, actually obtained in the course of routine control work, for seventeen different cakes, compared with those of samples prepared from the same bulks by grinding in a hand-mill, are instructive:

		Hand-mill		Christie & Norris mill	
		Albuminoids Per Cent.	Moisture Per Cent.	Albuminoids Per Cent.	Moisture Per Cent.
Ground-nut cake	No. 1	42·8	—	42·8	—
„ „	No. 2	44·0	8·0	43·9	8·2
„ „	No. 3	44·4	8·4	44·6	8·6
Cottonseed cake	No. 1	44·6	8·0	44·5	8·0
„ „	No. 2	44·2	8·6	44·4	8·6
„ „	No. 3	43·1	11·0	42·9	11·2
Soya-bean meal	No. 1	45·8	12·4	45·7	12·2
„ „	No. 2	46·7	10·8	46·8	11·0
„ „	No. 3	47·8	12·0	48·0	11·8
Linseed cake	No. 1	31·5	9·2	31·4	9·2
„ „	No. 2	33·8	8·8	34·0	9·0
„ „	No. 3	34·2	8·8	34·1	8·8
„ „	No. 4	33·5	8·4	33·6	8·8
Ground-nut meal	No. 1	55·5	—	55·4	—
„ „	No. 2	55·8	—	55·7	—
Rape meal		35·5	7·6	35·7	7·6
Pollards		16·5	12·2	16·3	12·2

We refrain from detailed comment on Dr. Elliott's figures, which, on the assumption of 3·6 per cent. loss in milling—his figure for hay—appear to indicate that the balloon attachment exercises a selective power on the albuminoid content, and causes the dispersion of matter containing over 100 per cent. of albuminoids.

The Influence of Amyl Ether on the indicated Fat Percentage in the Gerber Process

A New Test for the Suitability of Amyl Alcohol

By D. O'SULLIVAN, M.Sc., F.I.C.

This investigation arose out of the difficulties of a creamery with its supplies of amyl alcohol (for milk analysis) bought in the usual way in the spring of 1933. The first sign of trouble was the indication of 0·18 per cent. of fat in the skimmed milk, a reasonable anticipation being reduction to an indication of 0·05 per cent. or less for machines running well. The Gerber test, applied to machine-skimmed milks, cannot be expected to give strictly accurate results, but its indications can form a useful check on the working of the separators.

Preliminary Examination.—The alcohol in question had the following characteristics:—(i) Sp.gr. at 15·5° C., 0·814. (ii) Ten ml. with 10 ml. of hydrochloric acid (sp.gr. 1·16) gave a clear solution; the addition of 1 ml. of water caused a separation. (iii) Two ml., when dissolved in 20 ml. of cold 50 per cent. (by vol.) sulphuric acid and centrifuged, showed no oily layer or globules.

The results obtained in the Gerber process, with 1 ml. of amyl alcohol, from used and unused packages of the same creamery supply were compared with the result given by the laboratory stock alcohol, and with the fat-percentage determined in the same milk by the Röse-Gottlieb process, and the following results were obtained:

	Fat Per Cent.	Excess Per Cent.
Used	3·05	0·15
Unused	3·05	0·15
Laboratory-stock alcohol ..	2·9	Nil
Röse-Gottlieb	2·9	—

A separation of the interfering constituents by distillation was next attempted, a Le Bel and Henninger fractionating column being used. The various fractions were applied to the determination of fat by the Gerber process in another sample of milk, 1 ml. being used. Fifty ml. were distilled, and six distillates were collected in succession, each measuring about 7 ml.

	Fat Per Cent.	Excess Per Cent.
1st Fraction	3·5	0·05
2nd ,, ...	3·55	0·10
3rd	3·5	0·05
4th	3·5	0·05
5th	3·6	0·15
6th	3·7	0·25
Residue	3·9	0·45
Laboratory-stock alcohol ..	3·45	—

The reduction of the excess obtained in the Gerber process with the first four fractions, and its rise in the 5th and 6th fractions and the residue, indicated a method for the concentration of the undesirable constituents. A further sample (about 1½ l.) of the alcohol was, therefore, procured. With the Gerber test it gave the following result:

	Fat Per Cent.	Excess Per Cent.
This alcohol	3·6	0·2
Laboratory-stock alcohol ..	3·4	—

First Fractionation.—Five hundred ml. were distilled, a 4-bulb Le Bel and Henninger fractionating column being used, and fractions were collected until 400 ml. had passed over.

The various fractions and the residue were then tested by the Gerber process. (All temperatures are roughly corrected for the length of the emergent stem of the thermometer.)

Ml.	Boiling point °C.	Fat Per Cent.	Excess Per Cent.
0–100	124–131	3·5	0·1
100–200	131–131·5	3·5	0·1
200–300	131·5–131·5	3·5	0·1
300–400	131·5–132	3·55	0·15
Residue in flask	132–	3·75	0·35
Laboratory-stock alcohol		3·4	—

The residue was now distilled slowly through the fractionating column, and smaller fractions were collected:

Ml.	°C.	Fat Per Cent.	Excess Per Cent.
400–425	130·5–131·5	3·75	0·15
425–450	131·5–131·5	3·8	0·2
450–475	131·5–132	3·85	0·25
475–490	132–132	3·9	0·3
490–496	132–132·5	4·0	0·4
Residue		4·8	1·2
Laboratory-stock alcohol		3·6	—

The concentration of the undesirable constituent in the later fractions was here apparent.

The final residue was further examined as follows:

For fat: A drop placed on filter-paper evaporated completely in the air without leaving a stain. There was, therefore, no fat or oil present.

Acid value and Ester value.—For comparison, the acid value and ester value of the laboratory stock alcohol were also determined.

	Residue	Laboratory stock	Blank
Acid value	g.	g.	
Weight taken	1·33	1·33	—
$N/10$ sodium hydroxide solution, ml. ..	0·2	0·03	—
Acid value	0·8	Nil	—

Ester value 25 ml. of approximately $N/2$ alcoholic potash were now added, and the mixture was boiled under a reflux condenser for 30 minutes and titrated with $N/2$ hydrochloric acid.

	Residue	Laboratory stock	Blank
$N/2$ hydrochloric acid, ml.	22·11	22·18	22·22
Ester value, as amyl acetate	0·005	Nil	—

In the case of the residue, the titrated liquor was quite cloudy and threw up oily drops having an odour of pears. The figures have no positive significance, but indicate the presence of ethers, aldehydes or their variations, rather than esters.

Test for aldehydes.—The residue gave no reaction with Schiff's reagent or ammoniacal silver nitrate solution.

Test for nitrogen and sulphur compounds.—The residue was boiled down with metallic sodium and then charred and tested in the usual way. There was no reaction.

Test for halogens.—These were not present.

The presence of an ether, probably amyl ether, was therefore suspected, and on this assumption a second fractionation of the original was undertaken. Five hundred ml. were used, and the Le Bel-Henninger column was replaced by the more efficient Sydney Young type, lagged.

Second Fractionation.—The first fraction, boiling at 95° to 100° C., amounted to 4 ml., and consisted of two layers, which were separated. The upper layer gave the Schiff reaction for aldehydes, and had b.p. 101° C.

Mixed with laboratory-stock amyl alcohol to the extent of 10 per cent., it did not interfere in the Gerber process; thus:

	Fat in milk Per Cent.	Excess Per Cent.
Ten per cent. solution of upper layer of fraction in amyl alcohol	2·85	Nil
Laboratory-stock alcohol	2·85	—

It was probably an aldehyde. The lower layer was water.

Second Fractionation continued. Ml.	Boiling-point °C.	Fat in milk Per Cent.	Excess Per Cent.
4–100	130·5–132	2·85	Nil
100–200	132 –132·5	2·85	Nil
200–300	132·5–132·5	2·9	0·05
300–400	132·5–132·5	2·9	0·05
400–480	132·5–132·5	3·1	0·25
Residue	—	—	—
Laboratory-stock alcohol		2·85	

It is to be noted that the fractions from 4 to 400 ml. were fairly satisfactory for use in the Gerber process, and that the amount of the interfering constituent in the distillates was considerably reduced, as compared with the corresponding periods of the first fractionation, owing, presumably, to the more efficient scrubbing of the vapours in the Sydney Young column.

As it did not appear probable that a complete separation of the interfering constituent concentrated in the high-boiling residue in a form suitable for identification could be attained by fractional distillation alone, experiments were made with a mixture of commercial amyl ether and laboratory-stock amyl alcohol to devise a process of isolation. The amyl ether used was described by the makers as "a mixture of isomers of which iso-amyl ether is the chief." (No attempt has been made in this work to distinguish between the various isomeric alcohols and ethers.) Gerber cream-tubes were used. The first attempts at extraction of the amyl ether in amyl alcohol solution by mixing with cold 50 per cent. (by vol.) sulphuric acid and (*a*) olive oil, or (*b*) petroleum spirit (b.p. 40–60° C.) were not successful. Melted, filtered butter-fat gave a satisfactory and clean separation, as was shown by the increase in its volume when read against the scale of the cream-tube, but this separation was not quantitative.

The residue from the second fractionation was, therefore, treated as follows: Sufficient melted butter-fat to cover about 50 small divisions on the scale (10 divisions = 0·556 ml. of water, when measured cold) was poured into a Gerber cream-tube. Cold 50 per cent. (by vol.) sulphuric acid was added, and then 2 ml. of the residue. The whole was heated gently so as to melt the butter-fat, shaken, centrifuged and cooled in order to solidify the fat; the acid liquid was poured into a second cream-tube containing butter-fat, and the process was repeated in this second tube. Each 2 ml. of the residue was treated similarly. The solid-fat extracts were surface-washed with cold 50 per cent. sulphuric acid and then with water, and the fat was melted at a low temperature and transferred to a distillation flask. The combined butter-fat extracts were distilled in steam. The upper layer of the steam distillate, measuring 2·7 ml., was separated and redistilled.

This second distillate had the following characteristics:—Colourless; insoluble in water; soluble in alcohol, ether and petroleum spirit. It had the peculiar odour of amyl ether. Sp.gr. at 15° C., 0·784; n_D^{20}, 1·409; b.p., 170–172° C. These characteristics identify this liquid as amyl ether.

In order to eliminate the possibility that the amyl ether separated above might have been produced during the treatment of the residue with the acid, another portion of the amyl alcohol was subjected to a third fractionation. Five hundred ml. were distilled, a Sydney Young still-head (lagged) being used. By more careful attention to temperature-control, a small residue boiling above 132° C. was obtained; this was steam-distilled. On subsequent dry distillation a small amount (5·1 ml.) of amyl ether was separated. This showed that amyl ether was pre-formed in this alcohol.

An approximate estimate of the amount of amyl ether in the alcohol was made by diluting commercial amyl ether with amyl alcohol until the excess reading in the Gerber test was 0·2 per cent. A 2 per cent. solution of amyl ether gave the desired result.

A 2 per cent. solution of the separated amyl ether in the 100–200° C. fraction of the second fractionation gave an excess-fat reading in the Gerber process of 0·2 per cent., *viz.*:

	Fat Per Cent.	Excess Per Cent.
This 2 per cent. solution ..	4·15	0·2
Laboratory-stock alcohol ..	3·95	Nil
Fraction, 100–200° C. ..	3·95	Nil

The alcohol was, therefore, reported to contain about 2 per cent. of amyl ether, to which was due its disturbing effect in the Gerber process.

TESTS FOR THE SUITABILITY OF AMYL ALCOHOL FOR THE GERBER PROCESS.—A tribute to the trustworthiness of the Gerber process is the small amount of adverse criticism it has evoked since its inception, more especially considering that it is one of the most widely used of every-day chemical tests. Gerber himself had noted that a naked contact between the acid and the alcohol for any length of time gave too high readings for fat percentage, and recommended admixture in the order: acid, milk, alcohol. This has been standard practice. The variations of the error due to contact of acid with alcohol were investigated by Richmond and O'Shaughnessy.[4]

In 1905 Richmond and Goodson published a note on the incidence and disturbing effect of petroleum,[5] and later in the same year, Richmond published the result of an investigation of the composition of the "fat" separated in the Gerber process.[1] One point is of particular interest: "14·666 g. of the Gerber fat were steam-distilled, and a marked pear-drop odour was noticed in the distillate." Amyl ether has a pear-drop odour.

In 1923 Harvey and Harvey contributed a note on the separation of an oily layer on mixing even satisfactory samples of amyl alcohol with sulphuric acid and water.[6] In 1933 several notes appeared: from Houston,[7] Golding,[2,3] and More[8]—the last quoting van Haarst[9] and Siegfeld.[10]

Golding's experience with normal amyl alcohol,[3] using 1 ml. and the Gerber process, was confirmed, thus:

	Fat Per Cent.	Excess Per Cent.
Normal amyl alcohol ..	4·2	0·45
Laboratory-stock alcohol ..	3·75	—

A large-scale Gerber test was made with the normal amyl alcohol.

To avoid excessive charring, it was necessary to dilute the acid. Twenty ml. of water and 380 ml. of Gerber acid were mixed and cooled; 440 ml. of milk were floated on, and 40 ml. of normal amyl alcohol were added as a third layer. The flask was fitted with an air-condenser, and the contents were well mixed and allowed to cool somewhat, after which 40 ml. of clear butter-fat were added, and the whole was shaken again, transferred to a separator and allowed to stand. The acid layer was run off (an exact separation was not sought), and the fatty layer was transferred to a flask with a little hot water and steam-distilled. The upper layer of the steam distillate, measuring 2·5 ml., was dry-distilled from a small oil-bath. It yielded:

A small fraction—about 5 per cent.—boiling below 100° C., and with the odour of an aldehyde derived from amyl alcohol.
,, ,, ,, ,, 10 per cent.—boiling between 100 and 140° C. and smelling of amyl alcohol;
about 2 ml. of a clear liquid, boiling up to 170° C., and having the characteristics of amyl ether, as previously noted.

A sample of unsatisfactory amyl alcohol kindly supplied by Mr. J. Houston of the Department of Agriculture, Northern Ireland, was next investigated. Used in the Gerber test it gave an excess reading of 0·6 per cent. On fractional distillation about 75 per cent. came over below 132° C. The distillate and the residue were used in the Gerber process:

	Fat Per Cent.	Excess Per Cent.
Distillate	4·15	0·65
Residue	3·8	0·3
Laboratory-stock alcohol ..	3·5	—

These results showed that the sample was a different type of alcohol from that received from the Creamery.

A large-scale Gerber test, conducted, as in the experiment described above, with normal amyl alcohol, gave a steam-distillate, measuring 2·1 ml., which separated similarly, on dry-distillation, into fractions.

The laboratory-stock alcohol, treated by this process, gave a steam-distillate of only 0·2 ml., smelling of amyl ether. The indication is that the high results in the Gerber process when using the other two samples were due to the presence of amyl ether in the "fat."

NEW TEST.—As the ordinary "oily impurities" test did not give any oily layer or globules with the alcohols investigated, another procedure has been devised. It has served to distinguish between the laboratory stock alcohol (which gave no layer) and the following:—The Creamery alcohol; the Northern Ireland alcohol; 1 per cent. amyl ether in laboratory-stock alcohol; 0·5 per cent. amyl ether in laboratory-stock alcohol; 0·25 per cent. amyl ether in laboratory-stock alcohol; normal amyl alcohol (as purchased); and unsatisfactory alcohol (kindly sent to me by Dr. W. L. Davies, of the National Institute for Research in Dairying at Reading).

All these gave layers, and in each case, on completion of the test, the smell of amyl ether was noticeable. The test will probably be of general application, depending, as it does, on giving the alcohols the opportunity to be transformed to ethers under approximately the same conditions as in the Gerber test.

Mix equal quantities of Gerber acid (1·820–1·825) and water, cool and adjust to a specific gravity of 1·510 (about 18·6 *N*). Place 20 ml. in a Gerber bottle, add 2 ml. of the sample, insert stopper, mix and centrifuge. No oily layer or globules should appear. Invert the bottle in a beaker, keep it lightly stoppered, and heat in water to 80° C. for approximately 30 minutes. Centrifuge. No oily layer or globules should appear. Add 2 ml. of water, mix, cool and allow the bottle to stand overnight. Centrifuge. No oily layer or globules should appear. (The appearance of an oily layer is always preceded by cloudiness.)

SUMMARY.—Too high readings for fat-percentage in the Gerber process for the analysis of milk have been shown to be due to amyl ether; the ether is preformed in the amyl alcohol, or formed during the reaction, and extracted by the "fat."

The necessity for adding the acid, milk, and alcohol in the order given is emphasised.

The "oily impurities" test is valueless for the detection of amyl ether in amyl alcohol.

A modified procedure is suggested for the selection of suitable alcohol.

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PUBLIC ANALYST'S LABORATORY
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Some Cryoscopic Measurements of Indian Milk

By P. S. MACMAHON, M.Sc., F.I.C., AND L. N. SRIVASTAVA, M.Sc.

A REPORT from the Public Analyst's Laboratory, Rangoon (Bunce[1]), included some cryoscopic measurements of the milk of the cow and buffalo. Although the standard Hortvet procedure was not followed, the results indicated that cryoscopic methods were likely to prove a valuable means of solving the special problems of milk analysis peculiar to India and Burma.

In this part of India the chief disturbing factor is the use of buffalo's milk. There is only a small consumption of goat's milk, whereas the buffalo ranks with the cow as a domestic milch animal of the highest economic importance.

In a memoir published by the Government of the United Provinces (Macmahon, Gupta and Mukerji[2]) the comparative results of the analysis of over 1000 samples of the two kinds of milk are tabulated. In that investigation the buffalo milk throughout the seasons was shown to contain, on the average, 7·19 per cent. of fat and 9·43 per cent. of solids-not-fat, whilst, on the other hand, the composition of cow's milk closely approached European standards. The fluctuation in the principal constituents of the milk of individual animals was so wide as to render the imposition of analytical standards almost meaningless. Those ultimately laid down, *viz.* 3·5 per cent. of fat and 8·5 per cent. of solids-not-fat, based upon the lower limits of cow's milk, thus left plenty of scope for watering down the richer buffalo milk to the limiting composition required by the regulations. As the milk sold in these provinces is usually mixed, the analyst, unaware of its origin, is often faced with a problem of unusual difficulty in the detection of adulteration.

We thought it advisable to make some comparative cryoscopic measurements of milk derived from local sources, particularly in view of the differences between the climatic conditions prevailing in the United Provinces and those of Burma.

Some measurements have previously been made in different parts of India: a few with the milk from individual animals by Leather at Pusa in 1915, and some by Stewart and Banerjea[3] at Calcutta, in addition to those by Bunce at Rangoon already quoted.

Stewart and Banerjea found no difference in the average freezing-points of the two milks, and Bunce has proposed a higher limit of —0·550° C. and —0·560° C. for the cow and buffalo, respectively. These investigators did not use the Hortvet apparatus.

The measurements tabulated below were made with this apparatus, and the procedure conformed strictly with that laid down in the A.O.A.C.,[4] due attention being paid to the points frequently emphasised in the comprehensive work of Elsdon and Stubbs.[5]

The mixed-herd samples were obtained from the Military Dairy Farm, Lucknow, under the supervision of the officer-in-charge, and were invariably examined within a few hours of milking, so as to minimise the risk of development of undue acidity, even in the hottest weather. The acidity was checked from time to time, and found to be negligible for purposes of the test. The apparatus was found to give comparable results throughout the year, in spite of the great range of atmospheric temperature at Lucknow, which varied in this laboratory from 23·1° C. in January to 38·3° C. in June. The only drawback to its routine use is the heavy consumption of ether, especially in the hot months.

The following condensed table shows the results obtained with the milk from mixed herds, and also with the milk of a single animal of each kind milked on the premises:—

Range of freezing-point depression Δ	Number of samples	Average	Average of all samples	Average solids-not-fat Per Cent.
Milk from an individual cow:				
0·545 to 0·549	3	0·547		
0·550 to 0·555	34	0·552	0·552	
0·556 to 0·560	5	0·559		
Milk from mixed-herd cows (about 60 *in number):*				
0·545 to 0·549	7	0·548		
0·550 to 0·555	116	0·551	0·551	8·75
0·556 to 0·559	6	0·557		
0·560 to 0·578	5	0·565		
Milk from an individual buffalo:				
0·555 to 0·559	1	0·555		
0·560 to 0·565	32	0·562	0·562	
Milk from mixed-herd buffaloes (about 60 *in number):*				
0·555 to 0·559	17	0·558		
0·560 to 0·565	112	0·561	0·561	9·30
0·566 to 0·584	8	0·575		

The mean Δ for cow's milk was found to be 0·551° (as compared with 0·544 found by Elsdon and Stubbs in England) and 0·562° for buffalo milk, results which coincide with the smaller depressions found by Bunce (*loc. cit.*), and were suggested by him as working standards. In all cases the limits of fluctuation are narrower, and display a satisfactory constancy for purposes of application of the freezing-point method in India. We find the same average difference as Bunce between freezing-points of the two kinds of milk, *viz.* 0·01° C., although at a slightly different level. This small difference, representing less than 2 per cent. of added water, thus places in the hands of the analyst an invaluable means of testing milk, especially that of the buffalo when watered down to the "legal" standard. The freezing-point appears to be independent of the widely fluctuating values of the natural constituents of the milks of these two species of animal.

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Liesegang Rings

Methods of Analysis for the Determination of Silver, Chromate, etc., in Gelatin or Agar Gel

By E. B. HUGHES, M.Sc., F.I.C.

(*Read at the Meeting, April* 3, 1935)

INTRODUCTION.—At a recent meeting of the Society (April 3rd, 1935) an account was given of an analytical study[1,2] of Liesegang Rings and the theory deduced therefrom. As results of analytical investigations are incomplete without details of the methods employed, and as the methods may also have other applications (for example, the method for chromate in gelatin is equally applicable to the determination of chromium in food materials), the working details of the methods are here given.

PURIFICATION OF THE GELATIN (*For experiments with silver chromate*).—For experiments in which the concentration of silver is so small that the amount of it reacting with salts originally present in the gelatin may be appreciable, it is necessary to employ gelatin in which the chloride, particularly, is low in amount.

(*a*) *Ash-free Gelatin.*—Loeb's[3] method of preparing ash-free gelatin (extraction of mineral matter with 0·0078 *N* acetic acid in the cold) produces gelatin which gives only the faintest qualitative tests for chloride and for phosphate. Unfortunately, in the gel prepared from such gelatin, the solubility of silver chromate is much reduced, and only very poorly formed rings of precipitate can be obtained in it, very little improvement being effected, even when the *p*H of the gelatin is altered (the *p*H of this ash-free gelatin being at about the *iso*-electric point, 4·7); in the preparation of such gelatin there are probably other losses in addition to mineral matter. Gelatin so prepared was, however, useful for certain portions of the work.

(*b*) *Electrolytically Purified Gelatin.*—Electro-dialysis through parchment membrane was found not to be a very satisfactory method, but direct electrolysis of a gel gave gelatin of sufficient purity and of unimpaired quality with regard to ring-formation.

A block of a 10 per cent. gel is prepared in a rectangular jar, so formed as to leave a space at each end between the wall of the jar and the gel. When the gel has set firm these spaces are filled with distilled water, carbon electrodes (previously well-boiled and washed) are inserted, and the gel is submitted to electrolysis, the water being frequently tested and changed. Finally, the gel is melted to render it uniform. By this means the chlorine-content of 10 per cent. gel was reduced from 0·004 *N* to 0·002 *N*, which is low enough to be neglected in the experiments in which 5 per cent. gelatin is employed.

PREPARATION OF SAMPLES FOR ANALYSIS.—At the conclusion of the diffusion experiment the gel is removed from the tube by inserting a wire in contact with the glass and rotating the tube so as to free the gel, which is then forced out of the tube by blowing. The length of the gel is measured, and it is then cut into thin slices which are weighed and analysed.

METHODS OF ANALYSIS

(I) SILVER AND CHROMATE.—(*a*) If the amount of silver present in a sample is not less than the equivalent of 1 ml. of 0·05 *N*, the following procedure is satisfactory:

The slice of gel (1 to 5 g.) is dissolved in 5 ml. of 5 *N* nitric acid (cold), and made up to 50 ml.

Silver.—Twenty ml. of this solution, after the addition of a few drops of ether to prevent frothing, are directly titrated with standard ammonium thiocyanate solution (0·1 *N* to 0·02 *N*), with ferric alum as indicator; the gelatin does not interfere. If much chromate ion is present its colour may affect the determination of the end-point, but this can be overcome by reduction of the chromate by a drop or two of saturated sodium sulphite solution.

Chromate.—The usual procedure, as given for chromium in chrome leather (*Allen's Commercial Organic Analysis*, 5th Ed., V, 346), is satisfactory.

Typical Test Result.—

One g. of 5 per cent. gelatin, 0·0544 g. of potassium chromate and 0·0340 g. of silver nitrate.

Found: 0·0549 g. of potassium chromate and 0·0342 g. of silver nitrate.

(*b*) *Chromate*, in small amount, in presence of a considerable excess of silver, *e.g.* 0·002 *N* chromate ion and silver up to normal.

The method is based on that of Evans[4] for the determination of chromium in steel, using Cazeneuve's[5] reagent (diphenylcarbazide), and, as given here, is applicable to the determination of chromium in organic matter,* allowing of the measurement of 0·2 p.p.m. of chromium in 5 g. material; consequently the method is described in full detail.

The slice of gel is destroyed by heating with 3 ml. of concentrated sulphuric acid in a pyrex tube, 100 vol. hydrogen peroxide being added in small amounts (1 to 2 drops) and boiled out after each addition, until destruction is complete; or the destruction may be, with advantage, finished with perchloric acid (60 per cent.), as in (*c*). The solution is then diluted to about 50 ml., and the chromate ion reduced by addition of a few drops of saturated sodium sulphite solution. This reduction is necessary to avoid occlusion of chromate ion with the silver chloride in the next stage when the silver is precipitated by hydrochloric acid. The precipitate of silver chloride is separated by centrifuging and filtering, washed twice with dilute hydrochloric acid (1 in 10), and the filtrate and washings are evaporated to about 10 ml. This solution, with 3 ml. of concentrated sulphuric acid, is boiled down in a pyrex tube till fuming commences, when a few drops of 100 vol. hydrogen peroxide are added, and the liquid is again boiled to fuming, after which it is diluted to a suitable volume (50 or 100 ml.), and an aliquot part, representing not more than 0·05 mg. of potassium dichromate, is taken. This portion is diluted to 25 ml. and treated as follows:

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* The particular technique was evolved in these laboratories for the determination of chromium in chromatised ligatures.

A few drops of 0·1 *N* potassium permanganate solution are added, the liquid is brought to vigorous boiling, and more permanganate solution is added, drop by drop, until a permanent pink colour is obtained which is not destroyed by further boiling.

5 *N* sodium hydroxide solution is then added from a 10-ml. pipette until the solution is just alkaline (as indicated by a change of colour and formation of precipitate), and 5 ml. are added in excess. The solution is then boiled; if it does not then become green, more permanganate solution is added, drop by drop, during vigorous boiling, until the liquid is just permanently green. Care must be taken to avoid the addition of more permanganate than is necessary. The liquid is then cooled to room temperature, filtered through a sintered glass filter, which is washed with about 20 ml. of water, the total liquid, which should be green and quite clear, being collected in a 100-ml. Nessler tube (A).

A control solution, in another Nessler tube (B), is prepared by diluting 5 ml. of 5 *N* sodium hydroxide solution with 20 ml. of water, adding 1 drop of 0·1 *N* potassium permanganate solution and cooling to room temperature. The liquid in A is diluted to about 70 ml., and that in B to about 60 ml., and to each are added 20 ml. of 10 *N* sulphuric acid and 5 ml. of the diphenyl-carbazide reagent (0·1 per cent. in 25 per cent. acetic acid solution). The colour in A is then nearly matched in B by the addition of standard potassium dichromate solution (0·0005 per cent.); both liquids are then made up to the mark, and more standard potassium dichromate solution is added to B until the colours are exactly matched.

(*c*) *Silver* in small amount [too small for method (*a*), *e.g.* amount equal to 1 ml. of 0·001 *N* silver or less], with chromate ion in small amount, or in excess.

The method comprises separation of silver from the chromate ion by extraction with diphenyl-thiocarbazone (dithizone) and subsequent determination of the silver by Jelley's[6] colorimetric method.*

The slice of gel (about 5 g.) is put into a pyrex tube, and destruction is effected by heating after the addition of 1 ml. of concentrated sulphuric acid and 4 drops of 60 per cent. perchloric acid solution. The solution is then diluted to 50 ml. with water, 20 ml. of this being used for the determination of chromate ion and 20 ml. for silver.

Determination of Chromate Ion.—Method (*b*), previously described, is used.

Determination of Silver.—To the 20 ml. of solution one drop of saturated sodium sulphite solution is added to reduce chromate, 2 ml. of 50 per cent. citric acid solution are added, and the solution is made alkaline with 10 ml. of 5 *N* ammonia and washed into a separating funnel with about 10 ml. of water. This mixture is then extracted twice (or more often, if necessary, until the colour of the reagent remains unaltered) with 10 ml. of dithizone solution* (0·15 per cent. reagent in chloroform), and the bulked chloroform extract is twice washed with 20 ml. of water, placed in a pyrex tube (8 in. by 1 in.) and evaporated to dryness in a water-bath, the residue then being "destroyed" by heating with 1 ml. of concentrated sulphuric acid and 4 drops of 60 per cent. perchloric acid.

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* The reactions of diphenylthiocarbazone ("dithizone") were described by Fischer,[7] and its use for the determination of small amounts of lead was first suggested by Allport and Skrimshire[8] for the determination of lead in dyestuffs. Interest in the reagent was thereby stimulated, and it has since been the subject of considerable investigation, particularly by Fischer[9] and his co-workers. Nevertheless, the general utility of the reagent for the separation of metals preparatory to their determination does not yet appear to have been fully appreciated. It may be mentioned that a method has been developed in these laboratories for the determination of zinc in food materials by means of this reagent.

The resulting solution is transferred to a 50-ml. flask and diluted with water to about 20 ml., after which the procedure is according to Jelley's method from the stage of addition of bromine water.

Example.—0·2 g. of 5 per cent. gelatin containing 0·2 mg. of silver with 1 ml. of 0·1 *N* potassium chromate added.

Found: 0·202 mg. of silver.

(II) CALCIUM PHOSPHATE.—The method of Washburn and Shear[10] gave satisfactory results. The agar in the slice of gel (about 1 g.) does not interfere.

(III) MAGNESIUM CHLORIDE AND AMMONIA.—The magnesium, hydroxyl, ammonium, and chlorine were all determined from the same slice of gel (about 1 g.): first the OH by solution in acid and back-titration, then the NH_4, and the residue after distillation was made up to a definite volume and one portion taken for determination of magnesium and another for chlorine.

Handy's[11] method of titration of the magnesium ammonium phosphate was found useful when a large number of determinations had to be made.

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In conclusion I wish to express my thanks to Messrs. J. Lyons & Co., Ltd., for facilities to pursue this investigation.

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* The reagent should be free from copper.

Determination of Physiological Activity of Hemp Resin by a Polarimetric Method

M. N. GHOSE, B.Sc. AND S. N. BHATTACHARJEE

THE physiological activity of the hemp drugs (obtained from *Cannabis sativa*, Linn.), *viz.* charas, ganja and bhang is associated with their resins, although the chemical nature of the active principle is still unsettled. Personne (*J. Pharm. Chim.*, iii, 31, 46), by repeated distillation of the same portion of water from large quantities of hemp renewed at each distillation, obtained a volatile oil with a strong odour of hemp. He thought that this was the active principle of the plant and named it "cannabene." Kobert, in 1894, isolated from *Cannabis indica* a dark and oily liquid, which he called "cannabindone." Subsequently, Wood, Spivey and Easterfield (*J. Chem. Soc.*, 1896, 69, 539), while investigating charas, isolated a resinous substance boiling at 265° to 270° C. under a pressure of 20 mm. To this product they gave the name "cannabinol" ($C_{18}H_{24}O_2$). They considered it to be the only active ingredient of hemp. Frankel, however (*Arch. Exp. Path. Pharm.*, 1903, 266), claimed to have isolated the active principle of hemp as a pure, chemically well-defined body—a phenol aldehyde having the formula $C_{21}H_{30}O_2$. He termed this product "cannabinol," and suggested the term "pseudo-cannabinol" for the substance isolated by Wood, Spivey and Easterfield.

It has been ascertained, however, that the resin-content of a hemp drug is not a measure of its potency. Hemp resin is a complex substance, and attempts to isolate the active principle from it have not yet been successful. This is probably because the active principle is unstable and undergoes rapid oxidation. Hooper (*Pharm. J.*, 1908) evolved a chemical method for evaluating Indian hemp. He based his results on the iodine values of the dried alcoholic extracts of the drugs. Subsequently, however, the results of experiments in this laboratory proved that this is not always valid. Marshall and Wigner (*Pharm. J.*, 1911, 86, 739) also showed that there was no definite relationship between the iodine value and the physiological activity of different samples. Marshall and Wood (*Brit. Med. J.*, 1912, 2234) examined the acetylation method, and found that also to be of little value. The general opinion is that the only reliable method for determining the physiological activity of hemp drugs is to study their physiological action on animals, especially dogs, but animal tests are not always trustworthy, for the animal itself becomes immune by repeated administration of the drug.

Sudborough and Rao, in "Tests for Ganja and other Products of Indian Hemp" (1918), have described certain qualitative tests for hemp resin, but, since ganja several years old will respond to these tests, that they have no definite relation to the amount of active principle.

We have attempted to formulate a suitable method for determining the physiological activity of hemp drugs. It has been known for some time in this laboratory that charas and resin extracted from ganja are also optically active. A polarimetric method has been devised for the assay of the drug. As a result of experiments on a large number of resins extracted from samples of charas (the resinous substance that appears spontaneously on leaves, stems, inflorescences and fruits of the hemp plant *Cannabis sativa*, Linn.), it has been found that the specific rotation of the resin of good and fresh charas is about −105°, whilst that of older and inferior material is as low as −64°. Samples with specific rotation −95° have about seven-eighths of the normal potency, those with rotation −85° to −92° about three-quarters, and those with rotation −77° to −80° about five-eighths, and so on. The specific rotation for exceptionally potent charas has been found to be about −115°, but such samples are rare. The method for the determination of specific rotation is as follows:

Two grms. of the sample are boiled in a Soxhlet tube under a reflux condenser for about 4 hours with about 75 ml. of carbon tetrachloride. The carbon tetrachloride extract is shaken with about 10 grms. of fused calcium chloride, and is immediately filtered and made up to 100 ml. The rotation of the extract is determined at the room temperature in a decimeter tube. The percentage of resin in the drug is calculated by evaporating 50 ml. of the extract in a platinum dish and weighing the residue to constant weight at a temperature not above 90° C. The specific rotation of the resin of the drug is calculated by the following formula:

Resin Per Cent.	Ash Per Cent.	Other vegetable matter and moisture (by diff.) Per Cent.	"Specific rotation" $[\alpha]_D$	Opinion of experienced smokers
37·7	38·2	24·1	−114·8°	normal
35·6	36·5	26·9	−113·6°	normal
34·7	35·9	29·4	−109·8°	normal
32·6	37·2	30·2	−106·3°	normal
38·9	34·8	26·3	−106·0°	normal
36·7	38·5	24·8	−104·8°	normal
36·3	32·0	31·7	−104·3°	normal
37·6	37·2	25·2	−104·0°	normal
33·3	31·0	25·7	− 95·7°	7/8th normal
32·7	36·5	30·8	− 92·6°	3/4th normal
30·0	40·5	29·5	− 92·4°	3/4th normal
41·5	37·1	21·4	− 91·8°	3/4th normal
34·5	34·2	31·3	− 90·4°	3/4th normal
38·4	30·5	31·1	− 90·2°	3/4th normal
38·0	40·2	23·8	− 86·6°	3/4th normal
30·8	38·6	31·4	− 86·6°	3/4th normal
34·2	27·0	38·8	− 85·0°	3/4th normal
33·2	41·6	25·2	− 77·2°	5/8th normal
25·2	40·3	34·5	− 68·8°	5/8th normal
32·5	35·7	31·8	− 64·0°	1/2 normal

$$[\alpha]_D = \frac{100 \times 0{\cdot}3465 \times X^\circ}{C}$$

where $[\alpha]_D$ is the apparent specific rotatory power of the substance,
X the reading on the Schmidt and Haensch (Ventzke) sugar scale, and
C the concentration of the solution in grms. per 100 ml.

In the absence of a more suitable standard of measurement, the degree of intoxication which a smoker experiences under ordinary circumstances has been taken as the measure of potency of the drug. The standard coin in India is the rupee, divisible into sixteen annas; hence the smokers usually mention the strength of the intoxicants in terms of annas, or more frequently in couples of annas. Thus, according to them, full strength is sixteen annas, 5/8th strength is 10 annas, and so forth.

Four habitual smokers, unknown to one another, and aged 60, 45, 37, and 32, were supplied with the same sample to smoke at their usual hours. The next day their opinions were taken. They usually agreed with one another, and differences of more than one anna were rare. We have not taken into account their estimate to 1/16th unit.

The results obtained with a number of charas (hemp resin) samples are tabulated on p. 314.

Making allowances for the variability of opinion of even experienced smokers, it will be seen that the more active the resin the higher is its specific rotation.

The resin of ganja (the flowering tops of the female hemp plant which, like charas, are smoked in India for intoxication) was extracted with carbon tetrachloride, and its specific rotation was determined in 4 per cent. solution. The results of some experiments are tabulated below:

Resin Per Cent.	Ash Per Cent.	Other vegetable matter and moisture (by diff.) Per Cent.	"Specific rotation" $[\alpha]_D$	Opinion of experienced smokers
13·1	15·7	71·2	−95·2°	normal
15·5	14·0	70·5	−94·1°	normal
13·3	13·4	73·3	−93·6°	normal
13·8	16·2	70·0	−90·4°	normal
14·3	13·8	71·9	−90·2°	normal
15·5	14·7	69·8	−89·4°	normal
11·7	15·0	73·3	−80·0°	7/8th normal
15·0	13·5	71·5	−77·0°	7/8th normal
12·8	14·6	72·6	−75·1°	3/4th normal
8·4	16·2	75·4	−74·3°	3/4th normal
15·0	16·1	68·9	−69·8°	5/8th normal
11·6	16·1	74·6	−67·2°	5/8th normal
13·5	16·6	69·9	−60·0°	1/2 normal
13·0	17·5	69·5	nil	almost nil

The specific rotation of ganja of good quality may be taken as about −90°, and that of inferior quality as −60° or less. Samples with rotations of −77° to −80° are about 7/8th active; with rotation −75° about 3/4th; with rotation −67° to −70° 5/8th active, and so on. The rotation of very old samples, having the usual resin-content but very little physiological activity, is practically nil (*vide* the last sample above). It may be mentioned, in passing, that chlorophyll, which is usually present in appreciable amount in ganja of poor quality, interferes with the transmission of light through the polarimeter.

It thus appears that in both charas and ganja there is some definite relationship between the specific rotation of the drug and its physiological activity.

This investigation has been carried out at the Chemical Laboratory, Calcutta Custom House, and is published by permission of the Collector of Customs, Calcutta. We are also indebted to the Special Chemical Adviser, Central Board of Revenue, Government of India, for his interest in this paper.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DIRECT TITRATION OF SOLUBLE ORTHOPHOSPHATES WITH LEAD ACETATE IN THE PRESENCE OF DIBROMOFLUORESCEIN AS ADSORPTION INDICATOR

In a previous communication (Analyst, 1933, **58**, 331) I described titration methods, with lead acetate as the precipitant, for the determination of caustic alkalis and borates in the presence of a suitable adsorption indicator. I have also used lead acetate as the precipitant in the titration of oxalates (*Trans. Faraday Soc.*, 1932, **28**, 561, 565).

The method can also be applied to the direct titration of orthophosphates, in neutral or weakly acid solution, in the presence of dibromofluorescein as the adsorption indicator. The best results are obtained with 0·05 molar concentrations of phosphate and lead acetate, though accurate results may be obtained with 0·005 molar solutions. A 0·1 per cent. alcoholic solution of the indicator is employed.

The reactions involved in the titration processes can be represented by the equations:

(1) $2NaH_2PO_4 + 3(CH_3COO)_2Pb = \downarrow Pb_3(PO_4)_2 + 4CH_3COOH + 2CH_3COONa.$

(2) $2Na_2HPO_4 + 3(CH_3COO)_2Pb = \downarrow Pb_3(PO_4)_2 + 2CH_3COOH + 4CH_3COONa.$

(3) $2Na_3PO_4 + 3(CH_3COO)_2Pb = \downarrow Pb_3(PO_4)_2 + 6CH_3COONa.$

The acetic acid liberated in the first two titrations is too weak an acid to affect the accuracy of the determinations. The presence of mineral acids, however, must be avoided, owing to their solvent action on the precipitated lead phosphate. With an orthophosphate, such as Na_3PO_4 (which is strongly alkaline) or Na_2HPO_4 (which is slightly alkaline), the solution must first be neutralised with nitric acid; with NaH_2PO_4 (which is slightly acid) neutralisation is not necessary. The following account of the titration of disodium hydrogen phosphate explains the method:

The Titration of Disodium Hydrogen Phosphate.—Twenty-five ml. of 0·05 *M* disodium hydrogen phosphate solution are neutralised with 0·01 *N* nitric acid, with phenolphthalein as indicator, 3 or 4 drops of a 0·1 per cent. alcoholic solution of the adsorption indicator are added, and the mixture is titrated with 0·05 *M* lead acetate solution; the addition of the indicator imparts an orange colour and fluorescence to the solution. The titration is continued, with vigorous shaking, until a permanent pink colour is observed on the precipitate of lead orthophosphate.

If 0·005 *M* solutions of phosphate are employed, 1 to 2 drops of the indicator must be added to 25 ml. of the phosphate solution. It is very important not to add excess of indicator; in order to give a sharp end-point, a high proportion of the dyestuff present in the solution must be adsorbed on the precipitate at the end-point. As the orange fluorescence of the original solution has a pale red reflex, an excess of the indicator would render the true end-point rather uncertain.

The mechanism of the titration is as follows:

1. As the titration proceeds, the excess of $PO^{\equiv}$ ions is adsorbed on the surface of the precipitate of lead orthophosphate, to form the complex body $[Pb_3(PO_4)_2]PO_4^{\equiv}$.*

2. In the presence of a slight excess of Pb^{++} ions, the phosphate ions are displaced by Pb^{++} ions from the surface of the equivalent-body (*i.e.* the precipitate at the exact equivalent-point). The equivalent-body now becomes $[Pb_3(PO_4)_2]Pb^{++}$.*

3. This positively charged body repels the remaining free Pb^{++} ions, but attracts the negatively charged anions of the indicator; and, as a result of this deformation of the electron systems of the latter, the colour and tendency to fluoresce of the dyestuff anions are altered. The accompanying colour change renders the adsorption visible at the equivalent-point, and an accurate titration becomes possible.

Since the titration can be carried out in weak acid solution, it is possible to titrate phosphoric acid in this manner, although this would seldom be necessary, as accurate alkalimetric titrations are available. The titration is correct to 0·5 per cent.

An interesting fact was noticed in attempting to titrate a solution of metaphosphoric acid by this method: it was found that the amount of lead acetate required was three times the theoretical amount calculated for the formula HPO_3. It is a well-known fact that, in addition to simple metaphosphates, metaphosphates derived from polymeric acids, $(HPO_3)_n$, are known, where *n* may be 1, 2, 3, 4, or 6. It seems likely, therefore, on the basis of this experiment, that lead metaphosphate is derived from the polymeric acid $(HPO_3)_3$. (Cf. *Inorganic Chemistry*, T. M. Lowry, p. 432.)

The experimental results of a number of titrations are given below. The method of procedure was to prepare an accurate 0·05 molar solution of the phosphate by weighing the required amount of the purest analytical reagent and dissolving it in CO_2-free water. In preparing these solutions the hydrated salt was used in most cases, but, for convenience in comparison, the weights given in the table are expressed in g. per l. of the anhydrous salt. The 0·05 molar solution of lead acetate was standardised with 0·01 *N* NaOH (ANALYST, *loc. cit.*). It will be seen that the results are quantitative within an error of 0·2 per cent. Similar accurate results were obtained with 0·01 molar solutions.

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* It has been shown by Lottermoser (*J. prakt. Chem.*, 1905, **72**, 39; 1906, **73**, 374) that a precipitate which has been formed by the combination of oppositely charged ions, exhibits an electrical charge with respect to its saturated solution; the sign of the charge depends on the ion which is present in excess in solution. For example, in the presence of an excess of Cl^- ions a precipitate of AgCl exhibits a negative charge with respect to the solution, and a positive charge when Ag^+ ions are present in excess. This can only mean that these ions are adsorbed on the surface of the ion-lattice of the precipitate, and the complex bodies thus formed can be represented quite arbitrarily by the formulae $[AgCl]Cl^-$ and $[AgCl]Ag^+$. Consequently, in the presence of an acidic adsorption indicator, such as a fluorescein derivative, the negatively charged anions of the dyestuff are attracted to the surface of the precipitate when it is positively charged, *i.e.* when Ag^+ ions are present in excess; the characteristic colour of the indicator anion is thereby altered. This fact, among others, has been used by Prof. Fajans as the basis of his Theory of Adsorption Indicators.

In the formulae of the complex bodies occurring in the phosphate titration given above it should be realised that they do not represent definite compounds, but serve as a conventional representation of the states of the *surface* of the precipitate during the titration.

Phosphate	No. of ml. of 0·05*M* lead acetate required by 25 ml. of phosphate solution	Concentration of anhydrous phosphate in g. per l. determined	
		(*a*) By titration	(*b*) By weighing
NaH_2PO_4	37·5	6·00	6·00
Na_2HPO_4	37·4	7·08	7·10
Na_3PO_4	37·4	8·18	8·20
KH_2PO_4	37·5	6·81	6·81
K_2HPO_4	37·4	8·69	8·71
K_3PO_4	37·4	10·59	10·61
$NaNH_4HPO_4$	37·3	6·82	6·85
$(NH_4)_2HPO_4$	37·4	6·58	6·60

A. W. WELLINGS

LEAMINGTON COLLEGE

A NEW REAGENT FOR ELIMINATING THE INTERFERENCE DUE TO CALCIUM IN THE VOLUMETRIC FEHLING'S TITRATION FOR INVERT SUGAR

EYNON and Lane (*J. Soc. Chem. Ind.*, 1923, **42**, 143T) have shown that the presence of the alkaline earth metals, more particularly calcium, decreases the copper-reducing power of sugar solutions. They suggested precipitation with potassium oxalate to remove the calcium, and demonstrated that this was a satisfactory procedure.

In a recent number of the *Chemical Trade Journal* (November 16th, 1934, p. 358) some details are given of the production and use of sodium hexametaphosphate (Calgon) for water-conditioning. It has been suggested that Calgon ionises to two sodium ions and a complex of the formula $Na_4P_6O_{18}$, and that calcium can be substituted for sodium in this, giving $CaNa_2P_6O_{18}$, which is soluble. When an excess of Calgon is added to a calcium solution the calcium becomes inert and cannot be detected by any of the normal reagents.

Provided that Calgon would retain its identity in the presence of Fehling's solution, its use might allow of the determination of invert sugar in solutions of invert sugar containing calcium. A preliminary test confirmed this. Further, there was no lag in the end-point, as is the case when calcium is present. Accordingly, the following experiments were made:

A 0·5 per cent. solution of pure invert sugar was used to standardise the Fehling's solution under standard conditions, methylene blue being used as indicator. Varying quantities of Calgon were then added to the Fehling's solution immediately before the addition of invert solutions, obtained from pure sugar and molasses which were known to contain insufficient calcium to affect the titration. In no case did the presence of the Calgon affect the result.

Calgon added	Titration Ml.	Theory Ml.
40 ml. of a 1 per cent. solution	20·00	20·00
30 ml. of a 5 ,, ,, ,,	24·70	24·70
20 ml. of a 10 ,, ,, ,,	24·70	24·70
10 ml. of a 33 ,, ,, ,,	26·55	26·50

Sufficient N calcium chloride solution was then added to solutions of sugar and molasses to give a $N/100$ concentration of calcium in the titrating solution. Titrations were made, with and without the addition of Calgon. As only a small amount of calcium can enter the Calgon complex, an excess of the reagent (10 ml.

of a 33 per cent. solution) was used. In all cases interference due to the calcium was eliminated.

Finally, a series of molasses was obtained, all of which were known to contain calcium. Titrations with solutions of these were carried out in triplicate.

(i) Without removal of the calcium.
(ii) With removal of the calcium by potassium oxalate.
(iii) Without removal of the calcium, but with the addition of 10 ml. of a 33 per cent. solution of Calgon.

In the following table the figures in the second, third and fourth columns represent ml. of the inverted solution of the molasses:

Sweetening matter content of molasses Per Cent.	Titration (i) Ml.	Titration (ii) (oxalate separation) Ml.	Titration (iii) Ml.
75	26·70	26·50	26·55
70	28·90	28·30	28·35
	28·90	28·25	28·40
70	29·05	28·35	28·35
	28·95	28·15	28·25
50	38·50	37·70	37·65
	38·60	37·70	37·70
50	41·15	40·10	40·10
	41·25		40·10

From these results it is clear that the addition of 10 ml. of a 33 per cent. solution of Calgon to the Fehling's solution immediately before the addition of the invert sugar solution will satisfactorily eliminate any interference due to the presence of calcium.

I have to thank the Government Chemist, Sir Robert Robertson, K.B.E., F.R.S., for permission to publish this note.

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CHARACTERISTICS OF SANDALWOOD SEEDS AND SEED OIL (MYSORE)

Although there is an extensive literature on sandalwood (*Santalum album*), nothing has been published about the seeds, except by Watt (*Dictionary of the Economic Products of India*, Vol. VI, Part II), who mentions that they contain a fatty oil which is used by the natives for burning purposes.

Santalum album (N.O. *Santalaceae*) is an evergreen tree, which grows wild in certain parts of the Mysore State, Coorg, Coimbatore, and the southern parts of Madras. It grows at different altitudes from the sea level to about 4000 feet, and the trees in the forests vary in height from 12 to 35 feet. The total area of sandalwood plantations in Mysore and Coorg has been roughly estimated to amount to 5200 square miles. The tree bears fruit twice a year, and the dried seeds are of the size of a large pea. The seed kernels, which are edible, are rich in oil, and, as the pericarp is fairly soft, the kernel can be easily separated by hand. A plentiful supply of the seeds could be obtained during the seasons if proper measures for their collection were enforced. At present, however, they are left to rot under the trees, only a small quantity being collected and exposed for sale in the bazaars by a few druggists.

In view of the lack of analytical data concerning the seed oil, four samples of seed obtained from different localities in Mysore, and two from Kuppam in Madras, have been examined. In each case 1 kg. of the seed was crushed in a mortar, and the meal was extracted with petroleum spirit for 14 hours in Soxhlet extractors. From 44 to 49 per cent. of oil, ranging in colour from golden yellow to dark reddish-brown (according to the colour of the pericarp), was obtained.

The oil absorbs about 15 per cent. of its weight of oxygen from the air in 4 days, passing through an intermediate tacky stage and finally forming a thin, elastic skin. At higher temperatures the oil thickens, becoming very viscous, and ultimately gelatinises in a short period. When heated in the presence of driers for 64 hours in a thin film it yields a glossy unbroken film. The oil can be readily bleached by treatment with sulphuric acid and dichromate.

The unsaponifiable matter is a highly unsaturated resinous substance (Wijs iodine value about 300).

The results tabulated below were obtained by the methods suggested by Bolton in the latest edition of *Oils, Fats and Fatty Foods.*

	Locality					
	Sagar	Heggada Devanakote	Kolar	Bangalore bazaar	Kuppam	
					A	B
Wt. of 100 seeds, g.	13·6	14·2	13·4	12·7	15·0	14·6
Wt. of 100 seeds without pericarp, g.	6·6	6·8	6·0	5·7	7·3	6·9
Oil-content of seed, per cent.	47	48·5	46·4	43·9	49	48·5
Refractive index, n_D^{60}	1·4780	1·4760	1·4765	1·4770	1·4770	1·4780
Sp.gr. of oil at 25° C.	0·938	0·936	0·928	0·930	0·945	0·940
Saponification value	190	188	185	191	194	197
Iodine value (Wijs)	145	149	142	138	153	146
Acetyl value ..	23	23·5	21·8	20·4	22·9	24·3
Acid value (as oleic acid), per cent.	11	11·7	10·5	13·6	14·5	14·1
Unsaponifiable matter, per cent.	17·5	18·2	16·8	17·1	18·8	18·1
Nitrogen-content of seeds, per cent.	1·98	1·93	1·84	1·76	2·1	1·97
Nitrogen-content of exhausted seeds, per cent.	3·73	3·78	3·69	3·41	3·8	3·76

The mixed fatty acids had: Molecular equivalent, 285; iodine value (Wijs), 102; solidification pt. (titre test), 35° C. The "solid" fatty acids (40 per cent. of the total acids) had: Molecular equivalent, 278; iodine value, 10·5.

Promising results have been obtained in experiments on the use of the crushed seed (as a substitute for linseed) for a poultice material, and with the unsaponifiable matter as a vehicle for ointments. In two experimental trials, ¼ lb. of the soaked and crushed meal was given to cows with their usual fodder. They ate it readily and showed no indications of illness after 10 days.

I wish to thank Professor T. P. Hilditch for his advice and for suggesting a scheme for the further investigation of this oil.

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SHREDDED SUET: A NEW MATERIAL USED FOR COATING

In January last an informal sample of shredded suet was submitted to us. It was of very good appearance, the shreds evenly coated, fairly easily detachable from one another, and the packet contained no detached coating material.

The legend on the packet read as follows:—"Refined and coated with a specially prepared flour. Guaranteed free from preservative, colouring matter, rice or other starches, and to conform with the Food and Drugs Act. It is sold as a mixture consisting of Pure Refined Beef Suet enriched by the addition of about 12 per cent. of a pure food product introducing valuable proteins, carbohydrates and vitamins."

This led us to suspect soya bean meal, and we confirmed this by the microscope. We found the sample to be composed of

Soya bean meal ..	6·5
Fat	91·5
Water, etc.	2·0
	100·0

We passed the sample as genuine.

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Building Research

THE CORROSION OF LEAD IN BUILDINGS*

The causes of the various types of corrosion of lead that may occur in connection with building materials may nearly all be classified as due to contact with cement, timber or soil, but reference must also be made to the effect of elastic fatigue of the metal in accelerating its decay.

I. Corrosion caused by Cements and Mortar.—Superficial injury of lead damp courses in contact with mortar is relatively common, the lead becoming coated with patches of red powder, but complete destruction is rarer. Instances are also recorded in which lead pipes imbedded in soil have been partly converted into a mass of red and yellow lead oxide in alternating rings, which, according to Kohlmeyer (*Chem.-Ztg.*, 1912, **36**, 993) are periodic in character, the red rings (consisting of Pb_3O_4) representing the dry season of the year, and the yellow rings of PbO representing the wet season.

The general opinion of builders and plumbers is that cement is much more corrosive than mortar. This is supported by cases investigated at the Research Station, and is to be attributed to the more rapid carbonation of lime mortar than of cement mortar.

In past investigations into the causes of corrosion by lime and mortar it has been shown that calcium bicarbonate has no action, owing to the formation of a protective film. Slaked lime was found to cause rapid corrosion, whilst carbonated lime mortar afforded protection against solution of the lead.

A solution containing calcium carbonate, calcium sulphate, and 0·8 g. of calcium [as $Ca(OH)_2$] per litre, *i.e.* nearly saturated, caused rapid attack; hence the corrosive action of lime solution is not prevented by the presence of gypsum and chalk.

Heyn's observation (*Deutscher Ausschuss für Eisenbeton*, 1911, Heft 8), that gypsum protects lead from corrosion by water, but not from attack by lime solution, has been confirmed.

In experiments in which cleansed lead sheets were three parts immersed in various solutions and suspensions and subjected for a month to the action of a current of air free from carbon dioxide, the following comparative amounts of lead were found in the filtered liquids:

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* Technical Paper, No. 8. By F. L. Brady, M.Sc., A.I.C. Revised edition, pp. 25. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. 1934. Price 1s. 1d., post free.

	Weight of lead per 100 ml. g.
Distilled water	0·009
Saturated lime water	0·108
Portland cement suspension	0·183
High alumina cement suspension	0·012
Portland blast-furnace cement suspension	0·162

So long as the specimen is losing weight regularly and no surface deposits are being formed, the change of apparent weight in water can be used to calculate the rate of removal of lead, *i.e.* the rate of oxidation. The following rates of oxidation were calculated from results in which the air was bubbled through the solution at a controlled rate:

	Rate of oxidation per sq.cm. per hour Mg.
Distilled water	0·28
High alumina cement	0·10
Saturated lime water	0·42
Portland cement	0·46
Saturated lime water, specimen not cleaned, covered with oxidation film	0·53
Saturated lime water, specimen previously tested 3 days in tap water	0·31

The lower rate of corrosion in a suspension of high alumina cement, as compared with Portland cement suspension, was to be expected in view of the fact that the alumina cement contained no free lime.

When exposed freely to atmospheric weathering, or when immersed in water containing calcium bicarbonate, lead rapidly develops a protective film of corrosion product. The film does not, however, afford any useful degree of protection against contact with lime or cement.

Nature of the Products of the Interaction of Oxygen and Lead in presence of Lime Solution.—Attempts to obtain a solid compound of lime with lead oxide, a calcium plumbite, have failed, since the solution decomposes on evaporation. Solutions obtained in a series of tests were examined by ultra-filtration, and the ratios of CaO to Pb of the solutions, before and after filtration, were essentially the same. These results indicate that a true solution of lead oxide in lime solution is formed, and strongly suggest the formation of a chemical compound which is a calcium plumbite. A small proportion of the lead present appears to be in colloidal solution.

METHODS OF PREVENTION.—Coating the lead with bitumen or, better, with bitumen-impregnated felt, affords good protection. Lime mortar exposed to the air carbonates more rapidly than cement mortar, and is therefore to be preferred to Portland cement for bedding lead damp-courses, pipes or electrical conduits. Additions to cement mortar do not offer much prospect of usefulness. No pronounced beneficial result has been observed by incorporating sodium silicate with cement. Tests amply confirm the opinion as to the comparative harmlessness of high alumina cement. The replacement of pure lead by alloys containing small proportions of tin, antimony and cadmium deserves attention (see Building Research Special Report, No. 19).

The extent of protection afforded to "Compo" pipes must depend upon the thickness and continuity of the tin coating. In one case examined the coating was too thin to make the lead resistant to corrosion by cement.

II. Corrosion caused by Timber.—Serious corrosion is frequently caused where lead is used in contact with timber. The typical case of such contact is where sheet lead is laid over oak boarding. The attack of lead by oak is analogous to the Dutch process for the manufacture of white lead. The minute quantities of organic acids in the wood are sufficient to cause slow but progressive corrosion during a period of years. In this connection the possibility of corrosion of lead by acetic fumes from manufacturing processes should not be overlooked. Injury to the lead covering of glazing bars in the roof of a pickle factory was found to be due to this cause. The lead had softened and a deposit of white powder (identified as white lead) was present on the benches and the floor.

The following conclusions were drawn from the various cases investigated:

(i) With oak that is fairly well seasoned, corrosion is not appreciable in two months, provided that access of water is prevented.

(ii) Under moist conditions seasoned oak rapidly corrodes lead. As a preventive, bitumen felt is effective, but a bitumen paint may not afford protection.

(iii) Soft woods may cause appreciable corrosion of lead, but to a much less extent than oak.

(iv) The only hardwood tested—teak—behaved similarly to oak.

III. Corrosion caused by Soil.—Most soils are innocuous, but it cannot be assumed that, under natural conditions, combinations may not arise that will cause corrosion to occur with any type of soil—clayey, peaty or sandy. The decay of lead in soil usually leads to the formation of a white deposit of basic lead carbonate, sometimes containing lead chloride or traces of other lead compounds. Analysis of deposits examined by Leybold (*Dingl. polyt. J.*, 1887, **266**, 220) suggests that in those instances the corrosion was due to causes similar to those operating in the decay of lead by timber, and that the decay was due to dilute organic acids acting in the presence of moisture, oxygen and carbon dioxide.

Failures of lead pipe in made-up ground are known. Such ground may contain coal ashes with soluble salts, and also decaying vegetable refuse, so that different types of corrosion are possible.

To prevent possible troubles, the pipes may be laid in some corrosion-inhibiting substance, such as chalk, limestone or old, well-carbonated lime-mortar, or the pipes may be wrapped with felt strips impregnated with bitumen. The substitution for lead of suitable lead alloys will also prevent trouble.

International Vitamin Standards

We are asked to announce that the International Standards for vitamins A, B_1, C, and D are now available for issue to laboratories, institutions and research workers in Great Britain and Northern Ireland. These standards were accepted for international use at the Second International Conference on Vitamin Standardisation held in London in June, 1934, under the auspices of the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations.

The Conference recommended that they should be kept at the National Institute for Medical Research, Hampstead, N.W.3, which would act for this purpose as central laboratory on behalf of the Health Organisation of the League of Nations. The required quantities of each of the Vitamin Standards are now being sent to national central laboratories for subsequent local distribution in countries abroad.

The National Institute for Medical Research, London, will continue to supply the International Vitamin Standards for use in Great Britain and Northern Ireland. The standards for the Vitamins B_1 and D remain unchanged, and their supply at regular half-yearly intervals will be continued as before. The standard for Vitamin A has been changed, a pure specimen of β-carotene having been adopted in place of the impure preparation of carotene hitherto employed. The unit of Vitamin A remains unchanged, though it is now defined as the Vitamin A activity contained in 0·6 microgram of pure β-carotene. In accordance with the recommendations of the Conference, the β-carotene is issued in the form of a solution in oil, of which 1 gram contains 500 International Units. The quantity of this standard solution supplied to each applicant is approximately 5 grams, and, on account of the small quantity available, it can be supplied only at yearly intervals, and not half-yearly as formerly. It is suggested, therefore, that care and economy should be exercised in its use, and that subsidiary laboratory standards, exactly assayed in terms of the International Standard, should be prepared for routine work.

l-Ascorbic acid has been adopted as the International Standard for Vitamin C, the unit of activity being defined as the vitamin C activity contained in 0·5 milligram of pure *l*-ascorbic acid. A quantity of approximately 550 milligrams will be supplied to all laboratories, institutions and research workers in Great Britain and Northern Ireland, who require it.

It is requested that those laboratories, institutions and research workers in Great Britain and Northern Ireland who do not receive the standards at present, and who desire to receive any or all of them, will apply to the Director of the Department of Biological Standards, The National Institute for Medical Research, Hampstead, London, N.W.3.

Argentine Republic

DECREES OF THE MINISTRY OF LOCAL GOVERNMENT*

TOMATO CONSERVES

THE following Decree (No. 51,226, November 7, 1934) has been signed by the President of the Argentine Republic.

1. The name "Tomato Extract" shall be used to distinguish the conserve, obtained by concentration and sterilisation, containing not less than 16 per cent. of dry extract, free from sodium chloride.

2. "Single Extract of Tomatoes" shall contain from 16 per cent. to 28 per cent.; "Double Extract of Tomatoes," from 28 to 36 per cent.; and "Triple Extract of Tomatoes," not less than 36 per cent. of dry extract, free from sodium chloride. "Tomato Sauce" shall contain up to 16 per cent., and not less than 10 per cent. of dry extract, free from sodium chloride. No tomato conserve shall contain more than 5 per cent. of sodium chloride.

3. The proportions of dry extract specified in Section 2 shall be determined on homogeneous fractions of 2 to 3 g., which shall be submitted to continuous desiccation for exactly three hours in weighed glass crystallising vessels, with perfectly flat bottoms, and of the official pattern (diameter, 6 to 6·5 cm.; height, 1·8 to 2 cm.; thickness of walls, 1 to 1·5 mm.). The sample must be spread over the bottom of the vessel by means of a flexible spatula, so that the thickness of the layer shall not exceed 1 mm. From the total dry extract, calculated on 100 g. of the original sample, the amount of any sodium chloride present (determined by the usual methods) shall be deducted. A supplementary examination for substances extraneous to tomato pulp (adulterants, colouring matters, preservatives) shall be made.

4. Raw tomato conserve, obtained by pulping in the cold, shall be termed "Tomato Paste." It shall not contain more than 15 per cent. of sodium chloride.

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* Leyes, Decretos y Resoluciones, 2nd Series, 1934. Ministerio de Hacienda, Buenos Aires.

5. The Department of Commerce and Industry shall require the foregoing descriptive names to be printed in prominent, easily legible type on the labels of the containers.

6. Manufacturers of sauces and extracts shall send out their products only in tin containers lined with sanitary lacquer, labelled with the correct descriptions, hermetically sealed by soldering after sterilisation, and containing not more than 20 kg. net weight.

Tomato pastes may also be sent out in wooden casks, not containing more than 20 kg. net.

The use of containers made of other adequate materials may also be authorised, subject to the approval of the Department of Commerce and Industry.

PERMISSIBLE AMOUNTS OF SULPHUR DIOXIDE IN WINES

By Decree No. 40,904 the amounts of sulphur dioxide that may be added to wine are regulated as follows:

It is prohibited to send out, or expose for sale, wines containing more than 320 mg. of total sulphur dioxide, with an allowance of 10 per cent. to compensate for errors in adding the preservative on an industrial scale.

Wines classified as "Sauterne" or "Sauterne Type," by the National Chemical Board (Oficinas Quimicas Nacionales) are allowed to contain up to 450 mg. of total sulphur dioxide.*

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* Presumably, per litre, but the amount of wine is not mentioned in the Decree.—EDITOR.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Is the Amylase Test alone sufficient to indicate Permanent Pasteurisation? M. F. Bengen and E. Bohm. (*Z. Unters. Lebensm.*, 1935, **69**, 146–152.)—With milk which has been heated for 30 minutes to 55° C., the ammonium sulphate serum always fails to give a positive test for amylase (*cf.* Rothenfusser, ANALYST, 1930, **55**, 758; Kluge, ANALYST, 1933, **58**, 168), a violet colour being obtained. Heating of milk at 50° C., even for 2 hours, does not, however, destroy the amylase completely, a yellow colour being invariably obtained. Comparative measurements have been made of the times necessary for the sera of milks subjected to various heat-treatments to degrade the starch used in the amylase test. The temperatures and times of heating (and the colours observed) were as follows: Raw milk, not heated, 3·5 hours (yellow); 50° C. for 30 minutes, 3·5 hours (yellow); 50° C. for 60 minutes, 4·5 hours (yellow); 50° C. for 120 minutes, 5·5 hours (yellow); 55° C. for 15 minutes, 10 hours (reddish-brown); 55° C. for 30 minutes, over 20 hours (violet); 60° C. for 15 minutes, over 20 hours (violet); 65° C. for 5 minutes, over 20 hours (violet). From these results, in conjunction with those previously obtained, it is concluded that the amylase test alone is inadequate to indicate if a milk has been heated for a sufficient time to ensure "permanent" pasteurisation. Failure to find amylase by the test shows only that the milk has been heated to at least 55° C. When used together with the turbidity test (*cf.* Bengen, ANALYST, 1933, **58**, 699) and the creamometric test (*cf.* Orla-Jensen, ANALYST, 1932, **57**, 383), the amylase test is able to show if any departure from the procedure laid down for permanent pasteurisation has been in the direction of insufficient heating or in that of addition of raw milk. Failure to answer to the amylase test, coupled with response to the turbidity and creamometric tests, indicates milk which has been insufficiently heated at a temperature above 55° C. but below 63° C. On the other hand, response to all three tests indicates raw milk, either alone or mixed with heated milk.

For fresh milks the *p*H values lie between 6·8 and 6·75, and for pathologically altered milks values ranging from above 6·8 to 7·3 have been found; the values for the ammonium sulphate limiting serums agree to within about ±0·1 with those for the original milks. When applied directly to milks having *p*H values below 5·9 (degrees of acidity above 13), the amylase test either fails or gives indefinite results; if milk shows more than 10 degrees of acidity, this should be brought down to 6 or 7 before its behaviour towards the amylase test is examined. This test is applicable also to butter-milk. Addition of 10 per cent. of goat's milk to cow's milk renders the ammonium sulphate limiting serum turbid, and when more than 30 per cent. is added, the filtration is slowed down almost to stopping-point. T. H. P.

Microscopy of the Husks of the Principal Cereals. H. Härdtl. (*Z. Unters. Lebensm.*, 1935, **69**, 113–127.)—When cereal flours are boiled with dilute alkali hydroxide solution and the residue is washed with water, microscopic examination reveals the presence of fragments of transparent tissue, which do not appear to correspond with any described hitherto. These fragments are incapable of swelling and possess no structure resembling cellular structure. They are not lignified and are hence extremely pliable, so that they can assume the most varied shapes. A high magnification is often necessary for their identification. Descriptions and drawings are given of pieces of such tissue found in wheat bran, rye-meal and bran, barley-meal and bran, oat-meal and bran, and maize meal. The husks of cereals sometimes show lignified tissues. With wheat and rye, the extent of such lignification varies with the degree of ripeness of the corns. Unlike rye of good quality, shrivelled grains show no lignification, either in the intact grains or in the ground condition; a means of distinguishing between ryes of good and poor quality is thus furnished. The chemical nature of the cell-walls of the various tissues of the above cereals has been investigated microchemically with alkali hydroxide, zinc chloride and iodine, sulphuric acid, and phloroglucinol and hydrochloric acid. T. H. P.

Maize in South Africa. B. Segal. (*J. Chem. Met. Mining Soc. S. Africa*, 1934, **35**, 163–169.)—Maize is grown in the Union of South Africa in approximately the proportions of 66 per cent. of dent maize, 33 per cent. of flint maize, and 1 per cent. of *Zea mays everta* (pop corns), *saccharata* (sweet corns), *amylacea* (soft corns), and *tunicata* (pod corns). The main variety consumed in the Union is the flat white dent corn, and the yellow dent is used for stock and fowl food. Percentage analyses of the most important varieties are as follows:—(*a*) *Zea mays indentata*, white dent, and (*b*) *Zea mays indurata*, yellow flint; moisture, (*a*) 10·93, (*b*) 10·46; oil, (*a*) 3·04, (*b*) 3·01; protein, (*a*) 10·93, (*b*) 10·28; fibre, (*a*) 2·13, (*b*) 2·06; ash, (*a*) 1·18, (*b*) 1·01; pentosans, (*a*) 4·57, (*b*) 4·49; starch, by diff., (*a*) 67·22, (*b*) 68·69; total phosphorus, (*a*) 0·36, (*b*) 0·32; organic phosphorus, (*a*) 0·31, (*b*) 0·28; inorganic phosphorus, (*a*) 0·05, (*b*) 0·04; ash from kernel, (*a*) 1·18, (*b*) 1·01; iron in ash, (*a*) 3·88, (*b*) 3·38; iron in kernel, (*a*) 0·045, (*b*) 0·034; total protein, (*a*) 10·93, (*b*) 10·28; prolamin (alcohol-soluble), (*a*) 4·86, (*b*) 4·90; glutelin (alkali-soluble), (*a*) 3·10, (*b*) 3·10; globulin, (*a*) 0·38, (*b*) 0·10; methylpentosans, (*a*) 0·60, (*b*) 0·60; combined fatty acid in farinose, as percentage of dry starch, (*a*) 0·604, (*b*) 0·604. The analyses of maize oil, (*a*) freshly expressed, and (*b*) refined in the laboratory, deodorised, but not demargarinated, showed: Sp.gr. at 15·5/15·5° C., (*a*) 0·924, (*b*) 0·9225; n_D^{40}, (*a*) 1·4660, (*b*) 1·4658; saponification value, (*a*) 192·0, (*b*) 191·3; iodine value, Wijs, (*a*) 118·7; (*b*) 119·1; Reichert–Meissl value, (*a*) 4·20, (*b*) 0·20; Polenske value, (*a*) 1·20, (*b*) 0·37; acid value, as oleic per cent., (*a*) 3·12, (*b*) 0·05; ash, per cent., (*a*) 0·056, (*b*) 0·02; glycerol, per cent., (*b*) 10·34; unsaponifiable matter, per cent., (*a*) 1·85, (*b*) 1·45; mean mol. equiv. of fatty acids, (*b*) 279·5; titre of fatty acids, (*b*) 17·9° C.; iodine value of liquid fatty acids, (*b*) 143·0. The average percentage composition of Grade No. 4 (U.S. Official Grain Standards), the quality of maize most commonly used in the American industry, is: Moisture, 11·6; oil, 5·20; protein, 10·40; starch, 54·8; other carbohydrates, 14·33; fibre, 2·09, and ash, 1·52. The standard for this grade is: minimum weight per bushel, 49 lbs.; foreign matter and cracked corns, 5 per cent.; moisture, 19·5 per cent.; maximum limits of damaged kernels—heat damage, 0·5 per cent.; total, 8 per cent.

D. G. H.

Determination of the Extract in Wine. C. von der Heide and W. Zeisset. (*Z. Unters. Lebensm.*, 1935, **69**, 138–145.)—The direct determination of the extract of wine is subject to various errors, since, during the determination, acetic acid and its homologues are largely lost, part of the lactic acid is evaporated, malic acid is partly converted into malo-malic acid, the total acid-content diminishes considerably owing to ester-formation with the glycerol, and sugars are decomposed to some extent. When the residue obtained is dissolved in water to the original volume, the solution has a specific gravity markedly lower than that of the wine freed from alcohol. Indirect estimation of the extract from the specific gravity of the alcohol-free wine avoids these errors almost entirely. In different countries different tables are used for the relation between specific gravity and extract-content, but the values given by any one table are all comparable. With normal wines indirect determination gives higher (by 1·5 to 2 g. per litre) values than direct determination, but with wines adulterated with glycerol the reverse may hold. A series of measurements has been made on a 1931 Geisenheimer wine to determine the effects of various additions of glycerol and of lactic acid—the two commonest adulterants of wine—on the results of the determination of the extract. As the amount of glycerol added was increased, the difference between the direct and indirect extracts gradually diminished to zero and changed sign when 6 g. of glycerol per litre was introduced. Wines highly adulterated with glycerol yield residues which remain semi-liquid on the water-bath and in the drying-oven (at 100° C.), and solidify only on cooling.

The quantitative effects of glycerol and of lactic acid recorded by previous authors are confirmed. Addition of 1 g. of glycerol per litre of wine increases the extract, found indirectly, by about 0·6 g. per litre, and 1 g. of lactic acid per litre raises the extract by about 0·65 g. per litre. When both glycerol and relatively large amounts of lactic acid are added, the difference between the direct and indirect extracts differs little from that found when the glycerol alone is added. In the discussion of the above results, the usefulness of extract determinations made in both ways in judging of the genuineness of a wine is emphasised.

T. H. P.

Composition of Commercial Palm Oils. IV. Progressive Hydrogenation as an Aid in the Study of Glyceride Structure. A. Banks, H. K. Dean and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1935, **54**, 77–82T.)—The glyceride structures of two palm oils—a native Cape Palmas and a Belgian Congo plantation oil—have been studied as representative of the extremes so far observed in fatty acid composition. The component acids of the two oils were respectively: myristic, 1·6, 1·3; palmitic, 32·3, 41·4; stearic, 5·5, 4·7; oleic, 52·4, 42·9; and linolic, 8·2 and 9·7 per cent. The oils were hydrogenated at 80° C. to varying extents, and the glyceride structures of the products were compared by calculation (except where linolic acid was still present) from the iodine value of the hydrogenated fat and the ester-fractionation analysis of the acids in the original oil. In several cases independent ester-fractionation analyses were carried out on the acids from the hydrogenated oils. Each of the partially hydrogenated fats and the original oils were also oxidised with potassium permanganate in acetone in quantities sufficient to yield the fully-saturated glycerides in amounts adequate for ester-fractionation analysis of their component acids. Where desirable, fractional crystallisation of the fully-saturated glycerides was carried out, to which process the fully-hydrogenated fats were also submitted.

The Cape Palmas oil (*a*) and the Belgian Congo oil (*b*) contained approximately (in percentages): tripalmitin (*a*) 2·0, (*b*) 5·5; dipalmitostearin (*a*) 1·5, (*b*) 1·0; dipalmito-"oleins" (*a*) 16·5, (*b*) 29·5; monopalmitodi-"oleins," including any palmitostearo-"olein," (*a*) 66·0, (*b*) 58·0; tri-C_{18}-glycerides (tri-"olein," or stearodi-"oleins") (*a*) 14·0, (*b*) 6·0. Palm-oil contains both α- and β-palmitodi-C_{18}-glycerides and both α- and β-mono-C_{18}-dipalmitins. The symmetrical forms (β-palmitodi-"olein" or β-"oleo"-dipalmitin) predominate, but there is evidence of increasing proportions of the unsymmetrical configurations (α-palmitodi-"olein" or α-"oleo"-dipalmitin), as the total amounts of palmitic and C_{18}-acids in the whole fat tend towards equality. The proportion of the unsymmetrical forms is thus definitely greater in the Belgian Congo oil than in the Cape Palmas oil. Any differentiation between linolic, oleic and stearic glycerides as such is not possible by the progressive hydrogenation method, but the proportions of stearic acid in the original fat in both oils are more consistent with the tri-C_{18}-glycerides being stearodi-"oleins" rather than tri-"oleins," and it is probable that tri-unsaturated glycerides are not present in any important amounts. The glyceride composition of the Belgian Congo palm oil (and consequently of other plantation oils, and also of native oils of Lagos, Bonny Old Calabar, Nigeria, Cameroons, etc.) would thus be roughly: fully saturated 7 (mainly tripalmitin with 1 to 2 per cent. of dipalmitostearin); "oleo"-dipalmitins, 29; "oleo"-stearopalmitins, 6; palmitodi-"oleins," 52; and stearodi-"oleins," 6 per cent.

D. G. H.

Ucuhuba Fat. A. Steger and J. van Loon. (*Rec. Trav. Chim. Pays-Bas*, **1935, 54,** 149–157.)—Two samples were examined: (1) A commercial product, supplied as a granular, yellow mass, not completely soluble in petroleum spirit and containing resin; (2) a sample extracted from the ground kernels of *Virola surinamensis* Warb., and separated into purified fat and resin. The kernel formed 86 per cent. of the whole nut and weighed, on the average, 1·43 g.; the total extract (oil + resin) amounted to 71·3, and the resin to 6·2 per cent. of the weight of the kernel. Sample (1) yielded 6·4 per cent. of resin on purification. The constants were as follows:

	Commercial sample			Extracted sample	
	Total	Purified	Resin	Fat	Resin
Sp.gr. at 78°/4° C.	0·9016	0·8855	—	0·8882	—
Iodine value (Wijs)	17	12·3	40	10·9	—
Thiocyanogen value	10·4	8·6	—	—	—
Saponification value	221	229	209	224	180
Acetyl value ..	234	—	244	—	—
Acid value ..	26·5	20·7	about 100	8·4	—
Reichert–Meissl value	1·5	1·5	—	1·6	—
Polenske value ..	3·9	4·6	—	4·0	—
n_D^{50}	1·4525	1·4502	1·5084	—	—
n_D^{70}	1·4445	1·4431	—	1·4446	—
M.p. °C.	47	47	—	51	—

The constants of the fatty acids (still containing some of the resin) of the crude commercial fat, the purified commercial fat, and the extracted fat were, in order: Iodine value (Wijs), 9·7, 10·6, 9·7; thiocyanogen value, —, 8·1, —; n_D^{70}, 1·4312, 1·4310, 1·4322; saponification value, 236, 236, 236; mean molecular weight, 238, 238, 238; m.pt., 47, 47, 48° C. The percentage composition of the fatty acids was: lauric, 12·6; myristic, 63·2; palmitic, 8·4; stearic, 1·5; 9:10-oleic, 6·3; linolic acid, 2·8; resinous matter, 5·2. The resin is composed of fatty acids (including hydroxy-acids) or their esters, unsaponifiable matter, and probably a little wax-like material.

T. H. P.

Structure of the Cell-wall of Coffee. K. Täufel and H. Thaler. (*Z. Unters. Lebensm.*, 1935, **69**, 152–158.)—The cell-wall material of a Santos coffee containing 10·4 per cent. of moisture was obtained by extracting the coffee successively with ether and water, which removed respectively 16·1 and 31·3 per cent. of the original dry matter. The dry cell-wall material contained 0·43 per cent. of ash and formed 52·6 per cent. of the dry matter of the coffee, this being made up of: furfural, 1·6; loss on treatment with chlorine dioxide, 5·6; "glucose" constituent, 47·0 per cent. The "glucose" constituent contained: Mannan, 15·3; xylan, 1·8; and cellulose, 29·9. The matter lost on treatment with chlorine dioxide was not merely encrusting material, but comprised also protein and mineral matter. The figure given for cellulose represents actual cellulose and not "crude fibre."

T. H. P.

Carbon Tetrachloride in Chloroform. E. Host Madsen. (*J. Pharm. Chim.*, **1935, 21,** 246–247.)—For the identification of carbon tetrachloride in chloroform the Danish Pharmacopoeia uses the following method:—From a distilling-flask fitted with a fractionation column, 20 g. of the chloroform are distilled until about 1 ml. is left in the flask. One g. of this residue, when shaken with 150 g. of water, should dissolve completely. If 1 per cent. of carbon tetrachloride is present, a very slight opalescence is formed. With 2 per cent. the solution is definitely opalescent, and with 3 per cent. insoluble droplets can be seen. If the procedure is modified so that the residue is only 0·5 ml., and this is shaken with 150 g. of water, a definite opalescence is obtained in the presence of only 1 per cent. of carbon tetrachloride. S. G. S.

Biochemical

Biochemical Method for Determining Indigestible Residue in Faeces. R. D. Williams and W. H. Olmsted. (*J. Biol. Chem.*, 1935, **108**, 653–666.)—The non-digestible residue is defined as vegetable matter not attacked by digestive enzymes in the mammalian gut and consisting of lignin, cellulose and non-water-soluble hemicelluloses. For the determination of this, stools are collected and weighed. The wet weight is multiplied by 4, this amount of water is added, and the mixture is diluted to the nearest 25-ml. mark, transferred to a suitable ball-mill and ground for 20 minutes, or until the suspension will pass a 20-mesh sieve. Brisk rubbing may be necessary to sieve it. Into a 50-ml. glass-stoppered container are placed 25 ml. of the suspension, the stopper is inserted loosely, and the whole steam-sterilised at 15 lbs. per sq. in. for 30 minutes in order to kill the spores and to gelatinise the starch. After sterilisation, the material is cooled to below 50° C., and 20 ml. of bile-salt buffer solution, 5 ml. of pancreatin and sodium chloride solution and a few drops of toluene are added. The material is well mixed and incubated for 3 days at 45° C., with occasional shaking. The digest is filtered through a 125-mesh silk cloth, the digest being added slowly, with, at the same time, a stream of water from a wash-bottle. The residue is washed with 200 ml. of water, then with 50 ml. of hot ethyl alcohol, followed by 25 ml. of hot benzene and finally 25 ml. of ethyl ether. The residue is then transferred to a 50-ml. glass-stoppered container, which is placed in an oven at 70° C: for 2 hours, or until the residue is dry. To this prepared material 20 ml. of chilled 21·4 *N* sulphuric acid are added, and the whole is shaken briskly and put into an ice-box at 6°–10° C. The container is kept in the ice-box for 24 hours and shaken hourly (particularly during the first 5 hours). At the end of this time distilled water is added rapidly until the volume is 300 ml. (1·426 *N* acid). The mixture is heated and kept gently boiling under a reflux condenser for 3 hours. It is then cooled to room temperature, filtered through a loose layer of ignited asbestos in a Gooch crucible, and washed thoroughly with distilled water. The first 50 ml. of the washings are collected and added to the filtrate. The residue is further washed with 100 ml. of water, followed by adequate washings with alcohol, benzene and ether, then dried at 110° C., weighed, ignited, and re-weighed, and the loss of weight is calculated as lignin. The filtrate is neutralised with 50 per cent. sodium hydroxide solution to phenol-red and further diluted to 500 ml. The total reduction is determined by the Shaffer-Somogyi copper reagent (*J. Biol. Chem.*, 1933, **100**, 695). A portion (40 ml.) is fermented by the Somogyi washed-yeast procedure (*J. Biol. Chem.*, 1928, **78**, 117), and the non-fermentable reduction is interpreted on the xylose-arabinose curve and multiplied by the factor 0·88 to convert pentose to pentosan. The fermentable reduction is interpreted on the glucose curve and multiplied by the factor 0·90 to convert glucose to cellulose. The pancreatin and sodium chloride solution is freshly prepared each day. To 100 ml. of 8·5 per cent. sodium chloride solution, 10 g. of pancreatin (U.S.P.) are added, and the solution is shaken for 30 minutes and filtered. The bile-salt buffer solution is prepared by mixing 20 ml. of 0·2 *M* potassium acid phosphate solution, 23·4 ml. of 0·4 *N* sodium hydroxide solution, 6·6 ml. of water and 2·0 g. of sodium taurocholate. The *p*H on final dilution should be 8·0 without the taurocholate. S. G. S.

Excretion of Copper in Urine and Faeces and its Relation to the Copper Content of the Diet. S. L. Tompsett. (*Biochem. J.*, 1934, **28**, 2088–2091.)—The use of amyl alcohol in the determination of copper by means of sodium diethyldithiocarbamate, as recommended by the author (*Biochem. J.*, 1934, **28**, 1544) has been extended to the determination of copper in urine, faeces and diets. For urine, 50–100 ml. are boiled almost to dryness with 5 ml. of concentrated nitric acid in a Kjeldahl flask. To the residue 2 ml. of strong sulphuric acid are added, and heating is continued to drive off the nitric acid. The remainder of the organic matter is destroyed by perchloric acid. The digest is made up to a known volume with water, and an amount containing about 0·01 mg. of copper is taken (about 50 ml. urine). To this 5 ml. of 20 per cent. sodium citrate solution are added, followed by 2 ml. of 4 per cent. sodium pyrophosphate solution. The mixture is made alkaline to litmus with ammonia solution, and 5 ml. of amyl alcohol and 0·5 ml. of 2 per cent. sodium diethyldithiocarbamate solution are added. The whole is well shaken, and the amyl alcohol layer is removed, filtered and compared in a colorimeter with a standard containing 0·01 mg. of copper. For the faeces, 1 g. of dried material is heated with 5 ml. of concentrated sulphuric acid and 15 to 25 ml. of perchloric acid until all the organic matter is destroyed. The excess of perchloric acid is then removed, and the mixture is cooled and diluted to 100 ml. If any white insoluble matter is present, the digest is diluted to 20 ml. with water, 1 ml. of concentrated hydrochloric acid is added, and the whole is heated until solution is complete, after which it is diluted to 100 ml. A volume containing 0·01 mg. of copper (about 10 ml.) is treated as for urine, except that 5 ml. of the sodium pyrophosphate solution are used. In the case of the diets 10 g. of the dried material and 5 g. of copper-free sodium phosphate are ignited together in a silica basin at as low a temperature as possible. Final traces of carbon are removed by treatment with concentrated nitric acid and heating. The ash is dissolved in distilled water containing 5 ml. of concentrated hydrochloric acid, and the solution is diluted to 50 ml. The analysis is carried out in the same manner as for the faeces. It is found that an average daily diet for humans contains 2 to 2·5 mg. of copper, and that the urine contains 0·08 to 0·48 mg. per litre.

S. G. S.

Chemical Method for Estimating Epinephrine (Adrenaline) in Blood. J. C. Whitehorn. (*J. Biol. Chem.*, 1935, **108**, 633–643.)—The method depends on the use of silicic acid for the separation of epinephrine from other reducing substances, and also on a sensitive arsenomolybdic acid reagent for colorimetric assay. The reagent is not specific for epinephrine, which must therefore be purified by the silicic acid treatment. The arsenomolybdic reagent is prepared by dissolving 60 g. of crystalline sodium molybdate and 10 g. of crystalline sodium arsenate in 250 ml. of water. The solution is filtered, to the filtrate and washings 5 ml. of bromine water are added, and the liquid is diluted to 500 ml. For use, 100 ml. of this solution are mixed with 8 ml. of concentrated sulphuric acid. The silicic acid is prepared by mixing 20 g. of finely granular precipitated silica with 60 ml. of dilute (1:1) sulphuric acid in a 500-ml. flask. The mixture is boiled for 10 to 15 minutes, with constant whirling. When cool, the supernatant liquid is decanted, and the silicic acid is washed by decantation ten or twelve times with 100-ml. portions of water. The residue is finally filtered and dried on a Buchner filter. A solution of 5 g. of anhydrous sodium sulphite in 50 ml. of water is also prepared and centrifuged. Just before use 5 ml. of this solution are mixed with 35 ml. of dilute (1 : 1) sulphuric acid. In addition, a phosphate buffer solution is required, and this is prepared by dissolving 17·4 g. of dipotassium phosphate and 6·8 g. of monopotassium phosphate in 100 ml. of water and filtering the solution. The ultimate standard is epinephrine; but, as weak solutions of this are unstable, it is convenient to use catechol instead, $10m\mu$ of catechol giving a colour equal to that of $5m\mu$ of epinephrine. The stock solution is made by dissolving 1 g. of crystalline catechol in water, adding 20 ml. of a 10 per cent. solution of anhydrous sodium sulphite and 100 ml. of *N* hydrochloric acid solution, and diluting to 1 l. Just before use some of the stock solution is diluted (1 to 500) with 0·4 *N* sulphuric acid solution. Five ml. of this weak solution will then contain $10m\mu$ of catechol. For the determination 7 to 10 ml. of blood are taken from the animal and transferred *at once* to a flask containing 50 ml. of 3 per cent. trichloroacetic acid solution. More of the acid solution is added gradually until the blood is diluted 10 times, when the mixture is shaken vigorously, allowed to stand for a period of from 15 minutes to several hours and filtered. While the blood solution is standing, a calcium chloride tube (approximately 20 mm. × 200 mm.) is prepared by making three small indentations about 7 mm. below the bulb. Into the space between the bulb and the indentations a small plug of cotton or glass wool is fitted. The tube is then attached to a suction-flask, and 5 ml. of silicic acid are added. The flask is attached to a filter-pump, and an arrangement such as a Hoffman clamp is also used, so that the fluid can be drawn through the tube at the rate of 3 drops per second. The silicic acid is washed with water and small portions (1 to 3 ml.) of sodium sulphite solution until the rinsings are neutral to bromthymol blue. Fifty ml. of the trichloroacetic acid filtrate (5 ml. of blood) and 3 drops of bromthymol blue solution are placed in a small flask and neutralised with approximately *N* sodium hydroxide solution. As soon as the *p*H reaches 7 or more, 1 ml. of the phosphate buffer solution is added immediately. This solution is then poured into the adsorption tube and sucked through the silicic acid at the rate of 3 drops per second. The tube and the silicic acid are rinsed with three successive portions of 8 ml. of recently boiled and cooled distilled water. Air must not be sucked through the tube. The adsorption tube is then removed, and a clean, dry, 15-ml. centrifuge tube is placed in the filter-flask. The centrifuge tube is fitted with rubber tubing at the bottom, so that it comes well up into the neck of the flask. The adsorption tube is now replaced, and 5 ml. of 0·67 *N* sulphuric acid solution are added. The tube is twirled to suspend the silicic acid, and the suspension is sucked into the centrifuge tube. Into a test tube (A) 5 ml. of the solution from the centrifuge tube are placed. Into a second tube (B) 5 ml. of the 1:500,000 catechol solution, and into a third tube (C) 5 ml. of a solution containing no epinephrine, but of acidity 0·4 *N*, are also placed. Into each of three tall test-tubes (1, 2 and 3) marked at 25 ml., are pipetted 2 ml. of the arseno-molybdic acid reagent, and the tubes are placed in a boiling water-bath for 5 to 10 minutes. Five ml. of the sulphite and sulphuric acid mixture are added rapidly to tube A, and the solution is mixed quickly and poured into tube (1). Tube A is rinsed once with the resulting mixture, which is poured back into tube (1), and placed in the boiling water-bath for exactly 3 minutes. Tubes B and C are treated in the same way. At the end of 3 minutes the tubes are transferred to a beaker of cold water and allowed to stand for 15 minutes or longer. The standard solution is diluted to 25 ml. and compared with the undiluted unknown and blank in a colorimeter. If the material to be tested differs from the blank by less than 0·02 mg. per litre, it should be counted negative, for a difference of this amount can be attributed to variability in the blank when the same reagents are used. S. G. S.

Relative Biological Efficiencies of the Vitamin *A* and Carotene of Butter. R. G. Booth, S. K. Kon and A. E. Gillam. (*Biochem. J.*, 1934, **28**, 2169–2173.)—No difference has been found in the vitamin *A* activities of butter from Shorthorn and Guernsey cattle during summer, autumn and winter feeding. The vitamin *A* and carotene contents of the butter were determined spectrophotometrically, and it was found that these varied considerably in the two breeds, although the total biological activity was the same. From these results it has been possible to calculate that the vitamin *A* activity of butter is about six times that of the carotene when measured by its growth-promoting action. S. G. S.

Agricultural

Effect on Fruit of Fumigation with Hydrocyanic Acid. F. Beran. (*Z. Unters. Lebensm.*, 1935, **69**, 170–174.)—Zyklon-B, a commercial product largely used for the fumigation of fruit (*cf.* ANALYST, 1933, **58**, 775), consists essentially of hydrocyanic acid absorbed in a carrier (kieselguhr, etc.), but contains also an irritant which affects the mucous membrane, and thus gives warning of its presence. Irritants of lower and higher vapour pressures than hydrocyanic acid are used, the latter indicating the presence of the hydrocyanic acid at the beginning of the fumigation, and the former becoming perceptible only after its completion. Zyklon-B contains a little ethyl or methyl chlorocarbonate, but its main irritant is methyl bromoacetate. Experiments with apples show that fumigation for periods up to 2 hours with either hydrocyanic acid (12 g. per cu. metre) or methyl bromoacetate (0·2 g. per cu. metre) does not injure the fruit. When, however, the two compounds are used together, 40 per cent. of the fruit show damage after

1 hour (at 18° C.), 60 per cent. after 2 hours, and 80 per cent. after 3 hours. This result is found to be due to the fact that the methyl bromoacetate intensifies the respiration of the fruit, so that increased quantities of hydrocyanic acid are absorbed. The use of calcium cyanide preparations, which yield hydrocyanic acid under the influence of atmospheric moisture, is, therefore, to be preferred to that of products of the Zyklon-B type. T. H. P.

Determination of Mono-calcium Phosphate by means of Urea. C. W. Whittaker, F. O. Lundstrom and W. L. Hill. (*J. Assoc. Off. Agric. Chem.*, 1935, **18**, 122–127.)—The method is based on the reaction of urea with mono-calcium phosphate according to the equation

$$Ca(H_2PO_4)_2.H_2O + CO(NH_2)_2 = H_3PO_4.CO(NH_2)_2 + CaHPO_4 + H_2O,$$

and depends on the fact that urea phosphate is soluble in alcohol, whilst calcium hydrogen phosphate is not. There are three main operations: (*a*) the treatment of the sample with a large excess of urea to ensure that the reaction goes to completion, (*b*) the precipitation of the calcium hydrogen phosphate from the mixture by the addition of alcohol, (*c*) the determination of phosphoric acid in the solution of urea and urea phosphate. Details of the method are as follows: To the sample (2 g. for mono-calcium phosphate, or 4 g. for ordinary or double superphosphate), ground to about 100-mesh fineness, and contained in a 100-ml. volumetric flask, are added 50 ml. of urea solution (90 g. of urea in 100 ml. of water), and the liquid is shaken mechanically or intermittently by hand for 4 hours, after which it is diluted to 100 ml. and filtered immediately. To a 25-ml. portion of the filtrate are added 75 to 100 ml. of 95 per cent. alcohol, the mixture is well shaken and filtered, and the precipitate is washed with 300 to 350 ml. of alcohol. The filtrate is diluted to 500 ml. with water, a 25-ml. portion of this filtrate is evaporated to dryness, and the organic matter is destroyed by adding 5 ml. of hydrochloric acid and 25 ml. of nitric acid, and again evaporating to dryness, this process being repeated if necessary. The residue is dissolved in 10 ml. of nitric acid and a little water, and the solution is neutralised with ammonia and rendered slightly acid with nitric acid. After dilution of the solution to 75 ml. the phosphoric acid is determined according to *Methods of Analysis, A.O.A.C.*, 1930, **16**, 10(*a*). The P_2O_5 found, multiplied by 2, gives the P_2O_5 present as mono-calcium phosphate. With samples containing free phosphoric acid, this free acid must be determined separately by a suitable method (*J.A.O.A.C.*, 1934, **17**, 487) and subtracted from the P_2O_5 found. S. G. C.

Organic

Iodine Values of Linolenic, Linolic and Stearolic Acids by the Wijs and Rosenmund-Kuhnhenn Methods. Y. Toyama and T. Tutiya. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 32–35B.)—The Wijs and Rosenmund-Kuhnhenn methods for determining iodine values were applied to linolenic and linolic acids, as the commonest polyethylenic acids in vegetable oils, and to stearolic acid, which has a triple linkage. With the first two acids, excess of reagent in the Wijs method has little effect on the value, particularly with linolic acid (unlike the values obtained for the highly unsaturated sardine-oil acids), and in the Rosenmund–Kuhnhenn method the influence of excess of reagent is still less noticeable, although the iodine values are lower by this method [272 (Wijs), 264·6 (Rosenmund–Kuhnhenn) for linolenic, and 181 and 176·7, respectively, for linolic acid]. Taking into account values previously obtained with highly unsaturated acids, it is concluded that the Wijs method gives higher iodine values than the Rosenmund–Kuhnhenn method for the polyethylenic acids, and that the discrepancy between the methods increases with increase in the degree of the unsaturation, being largest in the case of the unsaturated acids of sardine oil and very small for linolic acid. With stearolic acid the Wijs method gives an iodine value corresponding to the absorption of 1 ml. of halogen, whilst results with the Rosenmund–Kuhnhenn method are influenced by the amount of excess of the reagent and are always higher than the value calculated for addition of 1 ml. of halogen. D. G. H.

China Jute Seed and Oil. T. Inaba and K. Kitagawa. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 77B.)—The China jute plant (*Abutilon avicenne* Garten; *Sida tiliafolia* Fisch. N.O. *Malvaceae*) is cultivated in Manchuria for the fibre. The weight of 100 seeds was 1·568 g., and their percentage composition was as follows:—Oil, 18·30; moisture, 10·29; nitrogen, 2·96; fibre, 14·03; ash, 5·55; P_2O_5, 2·56. The constants for the oil were: Sp.gr. at 15/15° C., 0·9281; n_D^{20}, 1·4769; saponification value, 190·3; iodine value, 139·0; acid value, 0·84; acetyl value, 16·3; Hehner value, 95·72; insoluble bromide, trace; unsaponifiable matter, 0·62 per cent. D. G. H.

Determination of Sulphuric Acid in Wool. J. Barritt. (*J. Text. Inst.*, 1935, **26**, 87–92T.)—A sample of carded, carbonised wool, weighing 2 g., is steeped in 100 ml. of distilled water in a tared flask, 10 ml. of 10 per cent. pyridine solution being then added and the contents of the flask made up to a suitable weight (*e.g.* corresponding with 150 to 250 ml.). The mixture is shaken well and allowed to stand for 1 hour, and suitable aliquot portions (*e.g.* 50 ml.) are removed and titrated with 0·1 *N* sodium hydroxide solution, with phenolphthalein as indicator. Details are given of the method of preparation of acid-free wool to which various known quantities of sulphuric acid were added in order to test the method, and it is shown that recovery is almost theoretical. Comparisons were also made with the terephthalic acid and triethanolamine methods (Trotman and Gee, *J. Soc. Dyers and Col.*, 1932, **48**, 321), but the results indicated that the acid was not distributed evenly throughout the wool. The pyridine method is preferred because, unlike the triethanolamine method, it is not empirical and does not give higher results with an increase of the excess of reagent, while the terephthalic acid method requires correction by a blank determination, and even then gives slightly low results. J. G.

Stains to Distinguish Fibroin and Silk Gum. W. S. Denham and E. Dickinson. (*J. Soc. Dyers and Col.*, 1935, **51**, 93–97.)—Sections are prepared (*cf.* Kultschicky, *Z. für wiss. Mik.*, 1887, **4**, 48) by winding 6 turns of raw silk on a wire frame and immersing them in a thick solution of "celloidin" in a mixture of ether and alcohol for 24 to 48 hours, followed by immersion for a few minutes in chloroform. When the solvent has volatilised the frame is embedded in paraffin wax (m.p. 130° C.), and sections 0·006 mm. thick are cut and, with the aid of warm water, are flattened on a slide smeared with glycerin-albumin. The slide is dried and washed in succession with xylene and a mixture of ether and alcohol to remove the paraffin and celloidin, complete removal being essential. Some of the silks were first degummed, and in this case a hank weighing 0·5 g. was treated in succession with 1 and 0·5 per cent. solutions of soap for 1 hour at 95° to 98° C., with an intermediate wash in warm water and a final wash in cold water. Poor results were obtained with 1 per cent. solutions of ruthenium red, although, after 5 to 20 hours, the gum had a deeper crimson shade than the fibroin. Picrocarmine (0·1 per cent. solution, 1 to 48 hours) gave a red to brown colour with gum silk, and yellow with degummed silk (*cf.* Wagner, *Melliand Textilber.*, 1925, **6**, 43, 118). Cyanine (quinoline blue) solution, prepared according to Herzog (*id.*, 1932, **13**, 121, 181) by dilution of a saturated solution to twice its volume with water, and then with one-third of the total volume of glycerin, gave deep blue and pale blue with gum and fibroin, respectively, after 2 hours. Azolitmin (0·1 per cent. of dye with 0·1 per cent. of sodium hydroxide for 24 hours) gave a blue stain with gum silk, but no stain with degummed silk (*cf.* Wagner, *loc. cit.*). Colours produced with 0·1 per cent. solutions of new stains are for gum and fibroin, respectively:—Benzopurpurine-4BS for 30 minutes, red to pink, pale pink to yellow; chlorazol purpurine-10BS for 30 minutes, orange-red to brown, pink; anthracene acid brown-G with 0·1 per cent. sulphuric acid for 30 minutes, golden brown, paler brown; diamine brown-B with acid for 30 minutes, chocolate brown, fawn; diamine green-G, with 0·1 per cent. sodium hydroxide solution for 45 minutes, dark green, pale green; acid magenta-N for 30 minutes, red-brown, blue-red; methylene blue-R (conc.) with alkali for 1 minute, blue-black, royal blue; alizarin delphinol-SEN for 30 minutes, dark green and light blue with hanks, and after 24 hours, blue-black and pale blue with sections. The results were similar for white or yellow hanks. Residual gum in degummed silk can be detected by means of azolitmin (which is slow in action), cyanine (which stains calcium soap and gum the same colour), benzopurpurine-4BS, picrocarmine, chlorazol purpurine-10BS and acid magenta-N. Beads produced by gassing are stained in the same way as sericin, but are easily recognisable by their shape. The results apply equally to white or yellow silks, but slight differences in shade are obtained according as hanks or sections are used. Addition of acid or alkali to the stain had either no effect or gave improved results (as indicated), but it should be avoided if possible with sections, as it renders manipulation more difficult. J. G.

Determination of Lignin. I. Errors introduced by the Presence of certain Carbohydrates. II. Errors introduced by the Presence of Proteins. A. G. Norman and S. H. Jenkins. (*Biochem. J.*, 1934, **28**, 2147–2159, 2160–2168.) —I. In the determination of lignin by the method involving the use of 72 per cent. sulphuric acid, several disturbing factors are present. The apparent lignin figure is increased by certain sugars, such as xylose and fructose, which give an insoluble residue when treated with 72 per cent. sulphuric acid. Polysaccharides containing pentoses and sucrose (presumably owing to its fructose unit) give similar residues. This disturbance has a time-factor, and at 2 hours the effect is small. Because of the presence of xylose, the figures usually quoted for lignin are too high, but this can be corrected, either by reducing the contact-time to 2 hours, or by pre-treatment with dilute mineral acids, although the latter method is of doubtful value, since the action of dilute acids on lignin is unknown. With pentoses the disturbance is probably due to the slow formation of furfuraldehyde and its condensation with lignin to form an insoluble phenol-furfuran resin.

II. Although proteins by themselves do not give a precipitate on standing with 72 per cent. sulphuric acid, yet, when they are added to vegetable matter, the lignin-content is apparently increased, and the residue contains nitrogen. This increase is probably due to the union of protein fission-products with lignin. If the nitrogen in the lignin is determined, calculated as protein, and a correction employed, an even greater error is often introduced. The reduction of the time of contact with acid from 16 hours to 2 hours, or the use of the Ritter–Seborg–Mitchell procedure (*Ind. Eng. Chem., Anal. Edit.*, 1932, 4, 202), does not reduce the error, but acid pre-treatment causes a reduction in most cases. When xylose and proteins are present together, treatment with 72 per cent. acid causes an insoluble precipitate to form if the amount of protein is small. As the amount of protein increases, the amount of the precipitate decreases, until, eventually, none is formed. The pre-treatment by acid hydrolysis is provisionally adopted. S. G. S.

Volumetric Method for the Determination of Free Sulphur in Rubber. A. F. Hardman and H. E. Barbehenn. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 103, 104.)—The method depends on the reaction of metallic copper with the sulphur in a medium of acetone, the copper sulphide produced being subsequently decomposed with hydrochloric acid, yielding hydrogen sulphide, which can be absorbed and determined volumetrically. The rubber sample (1 to 2 g.) is extracted with 50 ml. of acetone by boiling under reflux for about 6 hours, a spiral of copper gauze (obtained by coiling up a 18 × 0·25-inch strip of 40-mesh gauze), previously cleaned in boiling concentrated hydrochloric acid and dried, being present in the acetone during the extraction process. After removal of the acetone, the flask containing the sulphurised spiral, together with any copper sulphide which may have scaled off, is closed with a stopper carrying a thistle-funnel, a closed leading tube, and an exit-tube connected with an absorbing vessel containing 10 ml. of ammoniacal cadmium chloride solution (10 g. of cadmium chloride, 200 ml. of water, 300 ml. of concentrated ammonia); 20 ml. of concentrated hydrochloric acid are poured into the evolution flask, which is heated on a steam-bath for about 5 minutes until the copper sulphide is dissolved. The hydrogen sulphide is then swept through the apparatus by admitting a stream of air for 1 minute. The absorbing solution should remain ammoniacal. A sufficient quantity of 0·04 *N* potassium iodate-iodide solution, followed by 10 ml. of concentrated hydrochloric acid, is added to the absorbing solution, when the cadmium sulphide dissolves; the quantity of standard potassium iodate-iodide solution added must have been sufficient to insure that a permanent yellow colour, due to free iodine, remains at this stage. After 1 minute, the free iodine is back-titrated with 0·04 N thiosulphate solution, starch being used as indicator. In six test-experiments with 0·01 g. of elemental sulphur in the absence of rubber, results varying from 0·00990 to 0·01007 g., with an average of 0·01001 g., were obtained.

S. G. C.

Sulphate "Pictures" as a Means of Identifying Inks and Estimating the Relative Ages of Writing. W. Heess. (*Archiv. für Kriminologie,* **1935**, **96**, 13–17.)—The method is an improvement on that suggested by Heess, Mezger and Rall (*id.*, **92**, 107), and depends on the fact that the combined sulphuric acid contained in most inks gradually diffuses away from the ink-stroke into the surrounding paper over a long period of time. This penetration is rendered visible as follows:—The paper is bathed in a solution containing 5 per cent. each of lead perchlorate and perchloric acid, which produces lead sulphate from the sulphuric acid present in the paper, and, since this compound is insoluble in perchloric acid, fixes it in the fibres. The iron salts in the ink also dissolve, at a rate which depends on the age of the writing, in 5 to 30 minutes. Any aniline dyes present in the ink must then be decolorised by addition to the mixture of 1 drop of a 1 per cent. solution of potassium permanganate, excess of which is at once removed by the action of water saturated with lead sulphate and containing a few drops of a 10 per cent. solution of hydrazine hydrochloride. The liquid is then poured off, and the paper is immersed in lead sulphate water for 10 minutes, and then washed with distilled water. The specimen is finally immersed in a solution containing 0·5 per cent. each of sodium sulphide and potassium hydroxide, which converts the lead on the fibres into lead sulphide. The paper is then again washed in distilled water, and finally in conductivity water for 15 minutes. An application to a case of suspected false entry in a health-insurance register is described, and photographs illustrate the writing (1) after 9 months, showing a faint stroke of normal width with sharp contours; (2) after 21 months, showing a rather wider and more intense line with more diffuse contours; (3) after 23 months, showing a further stage in diffusion of the acid; and (4) after 45 months, showing a blurred line twice its original width. It is possible to distinguish (1) from (2), (3) and (4), and also (2) from (4), but not (3) from (4). It is desirable that the specimens compared should be written on the same paper, as this influences the degree of spreading. In the case of wood paper, which contains variable quantities of sulphate, this is particularly important. It is also essential that all the specimens should have been stored under the same conditions of temperature and humidity; an illustration shows writing on paper which is believed to have been stored in an unheated room and which appears less blurred than (4), although it is 42 months old. Examination of the specimens is facilitated by ensuring that the treated and untreated specimens are adjacent parts of a common line, and by the use of a lens. Photographs (magnification 10 to 15) are conveniently taken with the aid of the Leitz Macro Ring Illuminator with a Summar 24 or 35 lens, and the use of panchromatic plates is advisable if the blank portions of the paper itself have become at all brown as a result of treatment.

J. G.

Benzoyl Auramine G. A New Indicator for Kjeldahl Determinations. J. T. Scanlan and J. D. Reid. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 125–126.)—Benzoyl Auramine G is said to be a somewhat more satisfactory indicator than methyl red or cochineal for Kjeldahl titrations. Good results were obtained with 0·15 ml. of a 0·25 per cent. solution in methyl alcohol added to 100 to 300 ml. of solution. The colour-change from violet to pale yellow is sharp, owing to the narrow *p*H range (5 to 5·6) of the indicator. When observed in daylight, an intermediate grey colour occurs between the violet and the yellow, indicating a *p*H value of 5·4; by tungsten lighting, the grey is not observed, but the main colour-change shows as clearly as in daylight. A disadvantage of the indicator is that it hydrolyses slowly, so that it should not be added to the solution until it is ready for the titration, which should be completed without delay. The new indicator can be prepared by benzoylating the free base of Auramine G (British Colour Index, No. 655); details of preparation are given in the original paper.

S. G. C.

Inorganic

Reactions of Mercuric Iodide. E. Montignie. (*Bull. Soc. Chim.*, 1935, 2, 373–375.)—Mercuric iodide is converted into mercurous iodide when (1) heated with neutral sodium sulphite solution, (2) treated with stannous chloride, or (3) boiled with sodium formate solution. Mercury is precipitated if the iodide is treated with (1) hydroxylamine hydrochloride in presence of potassium hydroxide, (2) sodium hypophosphite in presence of hydrochloric acid, or (3) phenylhydrazine and zinc in presence of potassium hydroxide. Either mercurous iodide or mercury is obtained by the action of sugars on the iodide in presence of potassium hydroxide. When heated with dextrose, laevulose, arabinose or xylose (sometimes in the cold), the iodide yields mercury, whereas treatment with sucrose, mannitol or inositol gives a brown mixture of mercurous and mercuric iodides.

Silver nitrate readily decomposes mercuric iodide, yielding silver iodide and mercuric nitrate. Similar double decomposition occurs when the iodide is heated with solutions of alkali or alkaline-earth chlorides, or of the hydrochloride of aniline, pyridine, α-naphthylamine, benzidine or *o*-phenylenediamine. The only heavy metal chlorides reacting with mercuric iodide are stannous chloride (see above), and ferric chloride which, when heated, gives mercuric chloride, ferrous iodide and iodine. Cold sodium thiosulphate solution, either acid or alkaline, dissolves mercuric iodide with formation of the complex $I.Hg.S_2O_3Na$; when the solution is heated, the reaction $Na_2S_2O_3 + HgI_2 + H_2O \rightarrow HgS + HI + NaI + NaHSO_4$ proceeds rapidly in acid, and less readily in alkaline, solution. Potassium selenite or selenate does not react with mercuric iodide in an alkaline medium, but potassium tellurate is converted into the pale yellow basic mercuric tellurate, $HgTeO_4,2HgO$. Saturation of an alkaline solution of diethylmalonylurea (veronal) with mercuric iodide, followed by concentration on a water-bath, yields a white, crystalline compound, $C_{16}H_{22}O_6N_4Hg$. A similar reaction takes place with ethylphenylmalonylurea (gardenal), the compound $C_{24}H_{22}O_6N_4Hg$ being formed.

T. H. P.

Volumetric Determination of Iodine in Mercury Compounds. D. Köszegi and N. Tomori. (*Z. anal. Chem.*, 1935, **100**, 257–259.)—The iodomercurate complex is decomposed by the following procedure:—The solution (about 25 ml.) is boiled for 1 to 2 minutes with 10 ml. of 2 *N* potassium hydroxide solution and 3 ml. of 40 per cent. formaldehyde. The precipitate of metallic mercury is filtered off, and the filtrate is neutralised to phenolphthalein with 0·1 *N* nitric acid and titrated with silver nitrate solution. W. R. S.

Determination of Molybdenum in Steel and its Separation from Tungsten. W. Werz. (*Z. anal. Chem.*, 1935, **100**, 241–257.)—A critical study has been made of the determination of molybdenum in steel, and of the interference of tungsten. As regards the precipitation of molybdenum sulphide, the author confirms the fact that pressure precipitation with hydrogen sulphide is not necessary. The essential factor for complete precipitation is a very rapid current of the gas; this will quantitatively precipitate the metal, even from solutions containing phosphoric acid. Copper is the only other member of the hydrogen-sulphide group found in alloy steels; for its separation from molybdenum, the mixed sulphides are boiled for a few minutes with 20 ml. of 10 per cent. caustic soda. The filtrate from the copper sulphide is boiled with 5 ml. of ammonium sulphide solution, and the molybdenum sulphide is precipitated by excess of dilute sulphuric acid, collected, and ignited to trioxide.

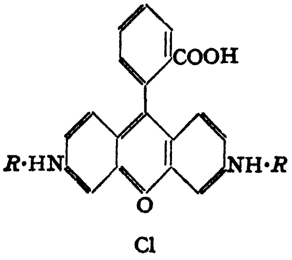
Separation from tungsten.—With alloy steels containing tungsten and molybdenum, the precipitated tungstic acid always contains molybdenum, whether nitric acid or chlorate has been used as oxidiser. Molybdenum cannot be quantitatively separated as sulphide in phosphoric acid solution from substantial amounts of tungsten such as occur in high-speed steels: the precipitate always contains more or less tungsten, while the filtrate is never quite free from molybdenum. When tungsten and molybdenum are separated from iron, etc., by addition of the solution of the steel to a strong solution of sodium hydroxide (a single treatment at boiling heat ensures quantitative separation from iron), and the acidified solution is treated with tartaric acid and hydrogen sulphide, the precipitated molybdenum sulphide is not free from tungsten. Correct results, however, are obtained by addition of the tartaric acid to the strongly alkaline solution (which should remain alkaline; an acid solution treated with tartaric acid must next be treated with excess of alkali). It must be assumed that a stable tartaro-tungstic complex forms in the alkaline medium. The solution is now acidified with sulphuric acid and treated at 80° C. with a rapid stream of hydrogen sulphide. By the use of this procedure it is possible to determine molybdenum in alloy steels without eliminating the iron. The drillings (1 or 2 g.) are dissolved in 20 ml. of strong hydrochloric acid and 30 of water, the solution is oxidised with 15 or 30 ml. of 5 per cent. potassium chlorate solution, chlorine is boiled off, and 30 or 60 ml. of 30 per cent. tartaric acid solution are added, followed by excess of hot 20 per cent. caustic soda. An excess of sulphuric acid is then added, the deep brown colour changing to green, the solution is filtered and diluted to 300 ml., and the molybdenum is precipitated at 80° C. by a brisk stream of hydrogen sulphide. The quantity of molybdenum in the assay should not exceed 0·03 g., otherwise its precipitation as sulphide is liable to be incomplete. For tungsten-free steels the procedure is as follows:—One g. of drillings is dissolved in water (20 ml.), strong sulphuric (10 ml.), phosphoric (5 ml.), and 1:1 nitric (10 ml.) acids; the solution is evaporated until white fumes appear, cooled, diluted to 200 ml., and filtered. The filtrate is treated with a rapid stream of hydrogen sulphide for 15 minutes, and filtered after 20 minutes' standing, and the precipitate is washed with hydrogen sulphide water acidified with sulphuric acid, and ignited to trioxide. Copper, if present, must be removed as described above. W. R. S.

Calcium Hypochlorite as a Volumetric Oxidising Agent. Determination of Ammonia. I. M. Kolthoff and V. A. Stenger. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 79–81.)—The calcium hypochlorite supplied by an American manufacturer yields solutions which are sufficiently stable for use as a volumetric oxidising agent; when kept in blackened bottles, 0·1 *N* and 0·01 *N* solutions suffered only a slight loss in strength in several months. An advantage of hypochlorite is that it may frequently be used for titration in slightly alkaline solution, thus eliminating interference by chromate, bromate, etc. The solution may be standardised (*a*) indirectly, by adding potassium iodide to it, acidifying, and titrating the liberated iodine with standard thiosulphate solution, (*b*) by using it to titrate 25 ml. of standard sodium arsenite solution to which has been added 10 ml. of a solution containing 10 per cent. of potassium bromide and 5 per cent. of sodium bicarbonate, 0·05 ml. of a 0·2 per cent. aqueous solution of Bordeaux dye being added as indicator near the expected end-point; the colour change is from pink to a faint yellowish-green. *Determination of ammonia.*—To 25 ml. of the neutralised ammonia solution are added 10 ml. of a solution containing 10 per cent. of potassium bromide and 5 per cent. of sodium bicarbonate, together with a slight excess of standard hypochlorite solution. After about 5 minutes, the liquid is decolorised by the addition of standard sodium arsenite solution, and then titrated with the standard hypochlorite solution, Bordeaux red being used as indicator. From 0·5 to 20 mg. of ammonia may thus be determined, 0·1 *N* hypochlorite solution being used for the larger quantities, and 0·01 *N* for the smaller amounts. In test experiments, results within 3 per cent. of the theoretical were obtained, and, when disodium hydrogen phosphate was substituted for the sodium bicarbonate as a buffer, the method was found satisfactory in the presence of about 30 mg. of copper chloride, ferric chloride and potassium bromate, and of 10 mg. of potassium dichromate. S. G. C.

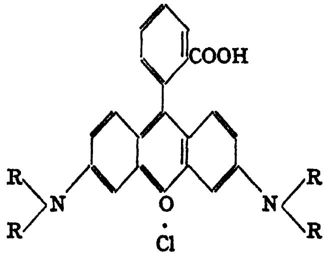
Rapid Test for Chlorate. H. R. Offord. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 93–95.)—A test-paper method has been devised for testing for chlorate in a few drops of solution. *Test-paper.*—No. 1 Whatman paper is soaked in 3 *N* ammonium thiocyanate solution and dried in a current of warm air at a temperature not exceeding 70° C. The dry paper may be kept without deterioration for several months if protected from light and dust. *Method.*—A drop of the solution to be tested is added to the paper, which has been dried before use at 60° C. for 10 minutes. The paper is supported on glass and placed in a drying oven at 95 to 105° C. for 5 to 30 minutes, the time required being the longer with small amounts of chlorate. A yellow colour is produced when chlorate is present. The use of duplicate test-papers is advised. The smallest detectable concentration of chlorate (either the sodium, potassium or calcium salt) was found to be 0·01 mg. per ml. The colour produced varies from a pale lemon-yellow (0·01 to 1·0 mg. per ml.), through a lemon-chrome (1 to 10 mg. per ml.), to orange or cadmium-yellow (over 10 mg. per ml.). The yellow colour is chiefly due to canarine ($C_3H_3N_3OS_7$) and pseudothiocyanic acid ($C_3HN_3S_3$). Chlorate in concentration of 0·1 mg. per ml. can be detected when present in 0·1 *N* solutions of sulphuric, nitric, acetic and oxalic acids, or sodium hydroxide, and also in acid or alkaline solutions containing 100 mg. per ml. of sodium chloride. Cyanide, thiosulphate and sulphite tend to interfere when present in quantity greater than the chlorate. The presence of any appreciable quantity of iron masks the test, and halogens, bromate, iodate, hypohalites, persulphate, peroxide (but not perborate) and cupric salts yield colours similar to that given by chlorate. *Application to plant extracts.*—Among tests carried out, it was found that chlorate in concentration of 0·05 mg. per ml. added to *Nitella* expressed sap was readily detected, the pale yellow colour of the sap itself not interfering. Positive results for chlorate were obtained in unfiltered or unclarified cold-water extracts of 1-g. samples of roots, stem, leaves and petioles of *R. petiolare*, when the plants had previously been soaked in dilute sodium chlorate solution, extracts of the untreated plants giving no interfering colour. S. G. C.

Microchemical

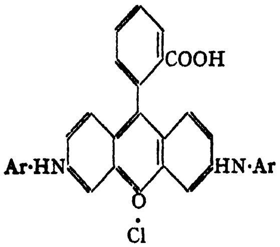
Spot Tests for Organic Compounds. VI. F. Feigl, V. Anger and R. Zappert. (*Mikrochem.*, 1934–35, **16**, 67–79.)—TEST FOR ALIPHATIC AND AROMATIC AMINES WITH FLUORESCIN CHLORIDE.—Many compounds containing the NH_2–, NH–, or NCH_3– group, when fused with fluorescin chloride and anhydrous zinc chloride, give dyestuffs of the rhodamine group. The nature of the dye varies with the different types of amines, and the reaction has been adopted as a test for their differentiation:—(i) *Primary aliphatic amines* and their salts give red dyes with yellow-green fluorescence of the general formula

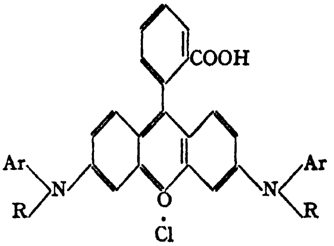


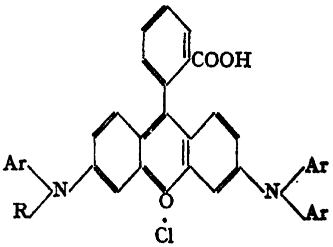
The fluorescence is visible by daylight as well as in ultra-violet light. *Method.*—A drop of the hydrochloric acid test solution is evaporated to dryness in a micro-test-tube or crucible, and the residue is mixed with a small amount of fluorescin chloride (as much as will lie on a knife-point) and double the amount of zinc chloride. The mixture is then heated in an air-bath at 250° to 260° C. until all the zinc chloride is melted. When cold, the melt is dissolved in 10 per cent. alcoholic hydrochloric acid, and, if the solution shows the fluorescence, a primary aliphatic amine was present. In the presence of only small amounts of amines the solution should be examined in ultra-violet light. For five different amines tested the identification-limit varied from 10γ to 30γ. (ii) *Secondary aliphatic amines* give rhomines with a red colour and orange-red fluorescence of the general formula:



The test is carried out exactly as described before. For diethylamine the identification-limit is 4γ, for piperidine 4γ, and for aceturic acid ester 20γ. (iii) *Aromatic amines* give dyestuffs of the following types according to whether they are primary, or secondary or contain a methyl group:

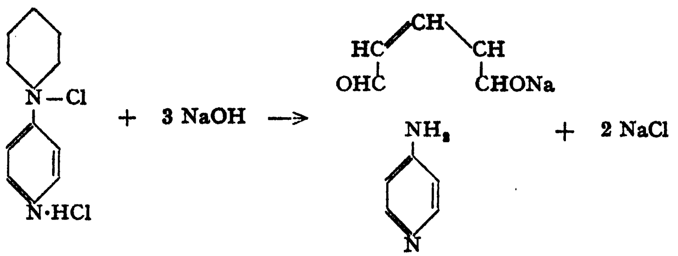






The alcoholic hydrochloric acid solutions of these dyestuffs are of an intense red-violet colour, but differ from the aliphatic amines in that no fluorescence is shown. The test is carried out as previously described. A table is given of 18 different amines, with the shade of colour and identification-limit (varying from 1γ to 400γ) in each case. (iv) *Acid amides and acid nitriles* react in the test in the same way as primary aliphatic amines. The test solution, however, must not be acid, but neutral, when evaporated to dryness. The fluorescence is yellow. The identification-limit for five different compounds tested varied from 20γ to 50γ. (v) *Pyrrole derivatives* react to form yellow-brown dyestuffs, which show a blue fluorescence in ultra-violet light. The test is carried out as already described, but the test solution should be evaporated in neutral or alkaline solution. Four pyrrole derivatives tested gave identification-limits varying from 12γ to 40γ.

TEST FOR PRIMARY AROMATIC AMINES WITH GLUTACONIC ALDEHYDE.—This is a modification of the "photo-pyridine reaction," Freytag and Neudert (*J. prakt. Chem.*, 1932, **135**, 15) and Feigl and Anger (*ibid.*, 1934, **139**, 180). Instead of pyridine, glutaconic aldehyde is used in the test; as this compound will not keep, the best reagent is 4-pyridyl-pyridinium dichloride, which liberates the aldehyde instantaneously in the presence of alkali.



Method.—Test-paper is impregnated with an alcoholic solution of sodium glutaconic aldehyde enol (prepared by adding 2 *N* alkali to a 1 per cent. dilute alcoholic solution of 4-dipyridyl-pyridinium dichloride) and dried, and a drop of the warm test solution in dilute mineral acid is dropped on to the paper. A red, violet or brown fleck is formed on the paper in the presence of amines, whilst a blank test gives a white fleck on the light brown paper. The test can also be carried out in a micro-crucible, a drop of the test solution, a drop of the 1 per cent. 4-pyridyl-pyridinium dichloride solution, and 2 drops of 2 *N* alkali solution being mixed, and then treated with 3 drops of 2 *N* hydrochloric acid. An intense red to violet colour, or precipitate, indicates the presence of the amine. A table is given of 14 different amines, the colour formed, and identification-limit in each case (0·05γ to 2γ). The reagent is prepared by the method of Koenigs and Greiner (*Ber.*, 1931, **64**, 1049). J. W. M.

Physical Methods, Apparatus, etc.

Conditioning-Box for Cloth Samples. A. W. Bayes. (*J. Text. Inst.*, 1935, **26**, 120–122T.)—The object of the box is to enable samples to be exposed to air at constant humidity before they are tested in the usual strength-testing machines. It should, therefore, be placed as close as possible to these machines, and provision should be made for the rapid removal of single samples without disturbing the humidity conditions in the box. The front of the box, the dimensions of which are 24 × 11·25 in. (height 13 in.), is made of glass, and immediately below the removable lid is an oblong piece of wood which divides the box longtitudinally; it also supports 50 cross pieces (25 on each side), into each of which is set a spring-clip type of clothes peg. Thus, if 5 specimens of warp and weft are taken from each sample, 5 samples may be conditioned together. Under the pegs are two photographic developing dishes containing a saturated solution of common salt and covered with small-mesh wire netting; one (11·75 × 10 × 2 in.) stands on the floor of the box, whilst the other (9·5 × 6·5 × 1·5 in.) is supported on a piece of half-inch board, and the rims are smeared with vaseline to prevent "creeping." The above solution is recommended, since, unlike an unsaturated solution of calcium chloride, it does not change in composition. It is cheaper than magnesium acetate, which has an inconvenient critical-point at which it changes to a wet cake, and it is more stable than ammonium nitrate. A circulating fan is not required, the humidity being 76 per cent. over the whole range of normal room temperatures, although it is desirable to suspend a paper hygrometer in the box just behind the glass front.

J. G.

Reviews

HANDBUCH DER LEBENSMITTEL-CHEMIE. A. BÖMER, A. JUCKENACK and J. TILLMANS. Vol. VI. FOODSTUFFS CONTAINING ALKALOIDS, SPICES, SALT. Pp. 604. Berlin: Julius Springer. 1934. Price, 76 RM., unbound; 79.60 RM., bound.

This volume treats of coffee, coffee substitutes, tea, maté, kola, cocoa, chocolate, tobacco, spices, and cooking salt, and includes the laws relating to these products. It deals with them with the encyclopaedic thoroughness which has been a feature of the previous volumes of this series, and gives an account of their chemical and microscopical characteristics with a wealth of detail not to be found in any other text-book. The photo-micrographs and drawings are particularly good, and the account both of the chemistry and of the technical production of the various substances is clear and well written. Methods of analysis are given in detail, usually with choice of various processes suited to particular circumstances. The subject-matter is brought right up to date, including references in 1933, but once again we would venture a mild protest against the scarcity of references to English scientific literature; it is annoying to an English reader to find reference to a page in the *Zeitschrift für Lebensmittel* (or other journal), and on turning this up to find that it is an abstract of a paper which appeared, say, in THE ANALYST or the *J.S.C.I.* This happens quite frequently, as, for example, the reference to the well-known paper of Tatlock and Thomson on tea—and could be avoided by giving the original reference to all non-German papers, as well as a reference to German abstracts. The cost of this series of volumes, at least in countries of the sterling bloc, is another serious factor. The present volume is excellent in many ways, and those who desire a really comprehensive treatise on foods will acquire it, but 76 RM. is too high a price for one volume—and that in paper covers.

In view of the work just published by Woodard and Cowland (too recent for inclusion in this volume) (ANALYST, 1935, 135), it is interesting to note the perpetuation of the statement that there is 7 per cent. of tannin in maté, although the authors truly point out that it is a peculiar tannin not precipitable in the ordinary way, as is tea-tannin.

Spices are very well described, and various types, such as capers, not to be found in most books, are included. Pepper in its many varieties is discussed in much detail. It seems at first curiously irrational, yet it is rational, to find salt, the composition of its many varieties, its impurities and methods for its testing, described in a volume devoted to alkaloidal foods and spices. But, in view of its importance in the food factory, its inclusion is justified.

We think this volume maintains the standard of thoroughness and excellence of its predecessors, but we do wish we could persuade its authors, as they wish us to buy it, to pay a little more regard to the convenience of English-speaking chemists.

H. E. Cox

ANNUAL REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY, 1934, Vol. XIX. Pp. 836. Published by The Society of Chemical Industry, 46/47, Finsbury Square, E.C.2. Price 12s. 6d. (to members 7s. 6d.).

This valuable annual, which consists of twenty-six reports, including, this year, the biennial report on "Explosives," fully maintains the standard set by its previous issues. The reports are the work of contributors of acknowledged eminence, who, by expert knowledge, wide outlook and considered opinion, have placed the miscellaneous information which the year's work has brought to light in its due relation to what has been established in the past and what may be expected in the future.

From the many subjects of interest to readers of THE ANALYST, space permits of the mention of only a few, but these, which are selected at random, will indicate the helpful nature of this publication.

In the report on "Glass" a resumé of a scheme for the analysis of clays is given. In the "Leather and Glue" report the difficulty of determining the *p*H value of tannery liquors is discussed—a problem by no means confined to these industries. The "Fermentation Industries" report includes a brief account of *r*H values, which are rapidly attaining the same practical importance as *p*H values. The "Iron and Steel" report contains a method for the rapid determination of silicon, based upon the colorimetric molybdate method used for its determination in waters. In the mass of highly interesting matter which forms the "Oils, Fat and Waxes" report will be found a method for the examination of olive oil removed from tinned sardines. The same report deals with such questions as the relation between the development of rancidity and the colour and composition of wrapping materials (a question also dealt with in the "Foods" report), and the factors affecting the vitamin-contents of butter and the fish oils. The "Fine Chemicals, etc.," report contains a summary of the existing knowledge of the chemistry of vitamins B_2 and C. The "Sanitation and Water Purification" section mentions the incidence of "mottled teeth" in districts where fluorides occur in the water supply, summarises a method for the estimation of fluorides and discusses the problem of their removal from drinking water (*cf.* ANALYST, 1934, **59**, 378, 380), whilst, from the "Fuel" report we learn that fluorine has been detected in coal in amounts sufficient to cause corrosion in gas-works scrubbers and to render the coal unsuitable for use in glass-bottle manufacture, and it is suggested that the source of the fluorine is infiltrated water.

Much information of absorbing interest is derived from journals familiar only to the specialist, and it is regrettable that a list of the full titles of journals indicated by abbreviated titles in the bibliography has not been included.

The very few misprints which occur lead neither to ambiguity nor to misstatement, and their corrected forms are obvious; consequently, they do not require enumeration. In the first line on p. 214 the word "peroxide," which should follow the word "sodium," has been omitted. The volume contains a name-index and an efficient, though not exhaustive, subject-index.

A prominent feature of the whole work is the easy narrative style adopted by each contributor, which makes this work not only a thoroughly competent, but also a genial and companionable guide for all those whose duty or pleasure it is to roam through the recent literature of Applied Chemistry.

A. O. JONES

THE SCIENCE OF RUBBER. By Prof. K. MEMMLER and CO-WORKERS. Authorised English Translation. Edited by R. F. DUNBROOK and V. N. MORRIS, in collaboration with the Research Staff of the Firestone Rubber Company (U.S.A.). Pp. 675, Bibliography and Indexes. New York: Reinhold Publishing Corporation. 1934. Price $15.00.

Memmler's *Handbuch der Kautschuk-Wissenschaft* was reviewed in THE ANALYST for January, 1931 (p. 71), and this authorised English translation follows closely the original German text. Several improvements have to be noted, however, not least of which is the valuable leavening influence of the American translators, who have brought the text up to date and inserted numerous references to the English and American literature. The addition of an extensive bibliography adds greatly to the value of the book for reference purposes, and author- and subject-indexes are provided.

As is to be expected with a composite work of this character, where separate sections are contributed by different individuals, the method of treatment differs somewhat from section to section, and this detracts a little from the readability of the book. The book unavoidably suffers in the same sense from the fact of translation, however well done.

The chapters or sections are not lettered and numbered as in the original German edition, but follow the same order, *viz.* Introduction; Botany, Cultivation, Collection and Preparation of Rubber; The Chemistry of Rubber; The Vulcanisation of Rubber; Chemical-Analytical Testing Methods; Physics of Rubber; Physical Testing Methods; and Microscopy of Technical Vulcanisates.

It is obviously not possible to read the whole of such an extensive book for review purposes, but a large number of tests have been made for reference purposes, and the treatise has come out with flying colours. For this reason, alone, it is likely to be found on the shelves of all rubber technologists.

A few small points noted by the reviewer may be mentioned. The illustration of Hevea particles on p. 54, which appeared in the German edition, will certainly strike most workers with latex as unusual, and one wonders how such a picture was obtained. In the botanical and plantation section fuller reference (with illustrations) should be made in future editions to the scientific aspects of the preservation and centrifugal concentration of latex for manufacturing purposes, which is only discussed briefly (p. 87). In the extensive section on the theory of vulcanisation (still the rubber chemist's most thorny problem) the translators, in inserting a note on the "reinforcement theory" of vulcanisation (p. 299, footnote), have missed the reference to the original contribution on this subject

(*Fourth Report on Colloid Chemistry*, 1921–22, p. 366; also *cf. J.S.C.I.*, 1928, 47, 37T, and 1929, 48, 60T), and might, perhaps, repair the omission in future editions.

The printing and paper of this book are excellent, although the cover, perhaps, is not attractive to English eyes; the price is adequate. W. H. STEVENS

METHODIK DER VITAMINFORSCHUNG. C. BOMSKOV, Ph.D. Pp. xvi+301. Leipzig: Georg Thieme. 1935. Price M. 24.

This is a very full account of the methods used by workers in different countries for making qualitative tests for vitamins. A little consideration has also been given to the quantitative estimation of these factors. Such details as the constitution of diets, duration of experimental periods and, in some instances, examples of results actually obtained, have been carefully quoted. Short accounts are given of the chemistry of the better-known vitamins, and reports of those vitamins whose existence is yet only suspected.

It is, however, to be regretted that so little attention has been given to the quantitative methods of estimation. The International Standards for the vitamins A, B_1, C and D are described in their respective sections, but there is no guide as to how the Standards should be used. An account of the general principles of biological methods of estimation would have been invaluable in this book. In particular, it might have been pointed out that it is absolutely essential to make a simultaneous test of the standard with every estimation which may be made of the vitamin-content of a substance. A closer search of the literature would have revealed the necessity for this procedure, and a realisation of its importance would have led the author to explain why such terms as the rat-growth unit, and the guinea-pig unit should *not* be used, and how impossible it is to convert any one of those units satisfactorily into International Units. The author, however, has not been critical; he has faithfully reproduced his findings in so far as his search has carried him.

The book is well printed and the illustrations are clearly reproduced.

K. H. COWARD

TABLE OF INCOMPATIBLES. R. L. WORRALL. London: John Bale, Sons & Danielson. Price 1s. 6d. net.

The Table of Incompatibles is printed on a sheet of good quality paper, approximately 17 inches by 15½ inches. It is intended for prescribers, and on one side are lists of oxidising and reducing substances, and acid and alkaline preparations which must not be prescribed together. On this side there are also lists of substances which should be prescribed alone, of those which may cause explosions, of those which decompose, and of those which deliquesce. On the reverse side of the paper 56 substances or groups of substances are depicted graphically on all four sides of a square. Black dots at intersecting lines indicate incompatibility, and open circles the possibility of incompatibility. The interest for the analyst lies in the fact that when a medicine is presented for analysis, any possibility of change in the ingredients due to interaction or decomposition, can, for most common substances, be readily detected, and the analytical procedure can be modified accordingly from the outset. S. G. STEVENSON

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9 JUL I.A.R. RES. PUSA

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 1st, Mr. John Evans, President, being in the chair.

The President referred to the loss the Society had sustained in the death of Leonard Archbutt, who was President in 1912 and 1913.

Certificates were read in favour of:—Francis Highland Milner, B.Sc., A.I.C., Lewis Charles Nickolls, M.Sc. (Lond.), A.R.C.S., D.I.C., A.I.C., Corbet Page Stewart, M.Sc. (Dunelm), Ph.D. (Edin.), Sidney Lionel Tompsett, D.Sc. (Lond.), Ph.D. (Glas.), A.I.C.

The following were elected Members of the Society:—William Godden, B.Sc., F.I.C., Frank Morton, B.Sc. (Lond.), A.I.C.

The following papers were read and discussed:—(i) "A Case of Meta Fuel Poisoning," (ii) "A Crystalline Putrefaction Product of Toxicological Significance," by G. Roche Lynch, O.B.E., M.B., B.S., D.P.H., F.I.C., and R. H. Slater, D.Sc., Ph.D., A.I.C.; "A Counting-Field Finder," by T. E. Wallis, B.Sc., F.I.C.; "A Colorimetric Method for the Quantitative Measurement of Rancidity," by Magnus A. Pyke, B.Sc.; (i) "The Determination of Total Alkaloids in Cocoa," (ii) "The Determination of Cocoa Matter in Flour Confectionery," by D. D. Moir, M.Sc., F.I.C., and E. Hinks, B.Sc., F.I.C.; "Colour Measurement of Oils and other Liquids," by E. R. Bolton, F.I.C., M.I.Chem.E., and K. A. Williams, B.Sc., F.I.C.

Obituary

ARTHUR JOHN STAREY

Although, in his earlier years, Arthur John Starey was frequently present at the meetings of our Society, he was personally known to but few of the present members. He joined the Society as an Associate in 1888, became a full member in 1899, and died on February 8th of this year, not long after he had become a life member under the new rule of the Society.

Apart from his professional activities (for 55 years he was associated with the firm of Messrs. Briant and Harman), he took a great interest in social work, was a great lover of children, and was never happier than when in the midst of young people. In private life he was a man of many interests. He served in the old Volunteers, and during the war was engaged in special constabulary work.

In 1896 he married Elizabeth, eldest daughter of William Macartney Read, of Silverton, Derbyshire, and is survived by three sons, one of whom (for many years resident in Australia) is a member of the Society.

EDITOR

The Chemical Examination of Furs in Relation to Dermatitis

Part V. The Action of Acid on Bandrowski's Base

BY H. E. COX, D.SC., PH.D., F.I.C., AND J. U. LEWIN, B.SC., F.I.C.

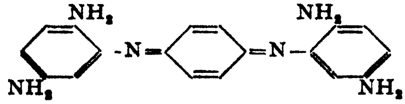
(*Read at the Meeting, February* 6, 1935)

IN an earlier paper (Part IV of this series[1]) it has been shown that when fur is dyed by the oxidation of para-phenylenediamine on the fibre, there is formed (in addition to the azine in and on the fur, which is the true pigment) a quantity of Bandrowski's base which is tenaciously held by the fur fibres, and, as is well known, there may be present small amounts of partly oxidised para-phenylenediamine. Although it is possible, by prolonged washing, to remove all trace of unoxidised para-phenylenediamine, the removal of all trace of Bandrowski's base is very difficult, and, in general, can be accomplished only by lengthy extraction with solvents. It is the purpose of this paper to describe quantitatively what happens when Bandrowski's base, or fur containing it, is treated with a mineral acid. The point is of considerable interest theoretically, because of the unusual reactions which are found to take place, and in analytical practice because both of the colour changes which might mislead the unwary and of the re-formation of the original diamine which, in fact, may not be present in the fur. When dyed fur from which all para-phenylenediamine has been washed out and which contains no Bandrowski base, is boiled with dilute hydrochloric acid (*N* strength), a brownish colour is produced, but no distinct red. Similarly, the azine itself, which is responsible for the dyeing, does not undergo any apparent change with acid; but if ordinary fur dyed by means of para-phenylenediamine is boiled with hydrochloric acid there is quickly produced a deep violet-red colour, which is due to the decomposition of Bandrowski's base. The colour closely resembles that obtained similarly from logwood or logwood-dyed fur, so that it is important to differentiate these two colours, and, as logwood-dyed furs are often topped with para-phenylenediamine, one must be able to detect quite small amounts of para-phenylenediamine in the presence of large amounts of logwood. Closely similar colours may be produced from the oxidation products of para-aminodimethylaniline; para-aminophenol and other common fur bases do not give reds, but only brown shades.

The decomposition of Bandrowski's base is but one example of the fission of a dyestuff, resulting in the formation of active intermediates. One frequently sees dyed fabrics or dresses in which the colour has been reduced by perspiration; it is our opinion that the products of the cleavage of azo dyes require careful study in connection with skin irritation. Forster[2] refers to this cleavage and regards it as a form of hydrolysis, as also do Rowe and Tomlinson[3] in the case of certain hydrophthalazines. The reaction with Bandrowski's base, however, appears to be more similar to the reductions effected by Wallach and Kölliker[4] by using hydrochloric acid. For example, by boiling 4-amino-azo-benzene with dilute hydrochloric acid they obtained aniline, para-phenylenediamine and some other compounds; the reactions were accounted for by assuming that hydrogen chloride acted like a mixture of free hydrogen and free chlorine.

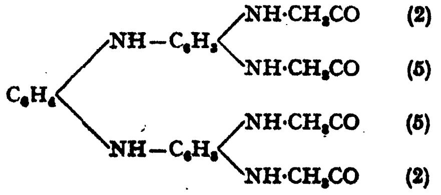
The point whether the splitting is to be regarded as a reduction or, as is more probably correct, as hydrolysis, is of minor importance compared with the fact of the splitting of such apparently stable compounds under the influence of dilute acid. Such an action may be of considerable physiological importance, in respect not only of dyed garments, but also of the possible effects of dyestuffs used in food manufacture.

Experiment shows that among the final products of boiling Bandrowski's base with dilute hydrochloric acid are:—much para-phenylenediamine, an insoluble black compound, ammonia, traces of carbon dioxide and hydrogen cyanide. Intermediate products include a bright red, unstable compound, which disappears on further boiling, and, possibly, quinone or hydroquinone. The structural formula of the base may be considered to be well established by the work of Heiduschka and Goldstein,[5] recently confirmed by Ritter and Schmitz[6]; it is



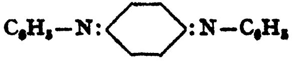
and, as is well known, it is formed by oxidation of para-phenylenediamine in alkaline solution; thus the point of interest and difficulty is to see just how it can split up and re-form para-phenylenediamine in the absence of any organic matter or added reducing agent. Of interest also is the liberation of hydrogen cyanide from a quinone linkage by so mild an agent as normal hydrochloric acid, and the production of ammonia, carbon dioxide and the red colour.

This action of hydrogen chloride is quite peculiar, for it has been shown[5] that when the base is boiled with acetic or sulphuric acid, acetyl or sulphuryl esters of the type



are produced, and these are stable compounds which can be isolated. Heiduschka and Goldstein tried hydrochloric acid, and record that they obtained a strong violet colour and a black substance, but were unable to isolate any compound.

We have isolated the black compound and found a formula for it, but have not been able definitely to isolate the red compound. It may be observed that red quinoneoid compounds of the type



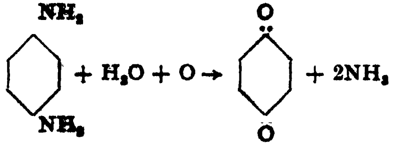
have been described by Willstätter and Piccard,[7] and others, such as Wurster's red, are well known. Jackson and Calhane[8] refer to a red, halogen-free hydrolysis product of para-phenylenediamine hydrobromide.

The details of an experiment show just what happens and the amounts of the various products. Five g. of dry crystallised Bandrowski base (which did not contain any cyanide or ferrocyanide) were boiled with 200 ml. of *N* hydrochloric acid under a reflux condenser for two hours; earlier experiments show that in this time the reaction is complete. One hundred ml. were then distilled into standard alkali to determine volatile acids (if any) and hydrogen cyanide (by silver nitrate). The presence of cyanide in the distillate was confirmed by the Prussian blue reaction. Ammonia was determined in another fraction, and carbon dioxide in a separate experiment by absorption with baryta. The para-phenylenediamine was determined in the liquor by precipitation as the dichlordiimide, and the residual black substance was washed, dried, weighed and subjected to elementary analysis by combustion. There was also evidence of a small trace of quinone. (No other compounds could be detected.) Here is the balance sheet:

Bandrowski Base			
5·00 g. = N 1·32 g.	Black substance	2·49 g. =	N 0·30 g.
	p-Phenylenediamine	2·00 g. =	0·56 g.
	Ammonia	0·47 g. =	0·39 g.
	Hydrogen cyanide	0·01 g. =	0·01 g.
	Carbon dioxide	0·04 g. =	—
1·32 g.			1·26 g.

The black powder, after thorough washing and drying, showed no definite melting-point; it is nearly insoluble in water, acids, pyridine, benzene and other organic solvents, and on analysis* was found to contain: C, 62·9; H, 4·8; N, 12·1; O, 20·2 per cent. These figures correspond quite closely with the composition $C_{12}H_{10}N_2O_3$. It seems clear that there are three oxygen atoms to two of nitrogen—a consideration which fits in with the supposition of a quinone-type compound, such as may be derived from re-oxidation of liberated para-phenylenediamine or quinone diimine.

It will be recalled that Green and Johnson[9] showed that when para-phenylenediamine is oxidised in acid solution, the yield was 95 per cent. of quinone, 5 per cent. being destroyed by further oxidation; they do not record whether any cyanide or carbon dioxide was sought for.

(1)


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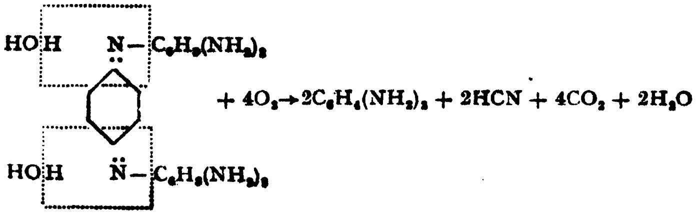
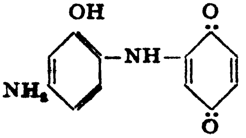
* We are indebted to Dr. H. D. K. Drew, who kindly carried out this combustion.

When one boils a mixture of para-phenylenediamine and quinone with dilute hydrochloric acid the products are of the characteristic red colour, and contain ammonia and a little carbon dioxide, but no cyanide. The production of hydrogen cyanide from Bandrowski base is a small side-reaction which can be due only to the rupture of the quinone group. This might be thought to leave a carboxylic acid or a ketene, but, as careful search failed to detect any such substance, it seems certain that the molecule has completely broken down into carbon dioxide and water; there is thus formed an amount of carbon dioxide which corresponds with the amount of cyanide actually found. This reaction probably proceeds thus:

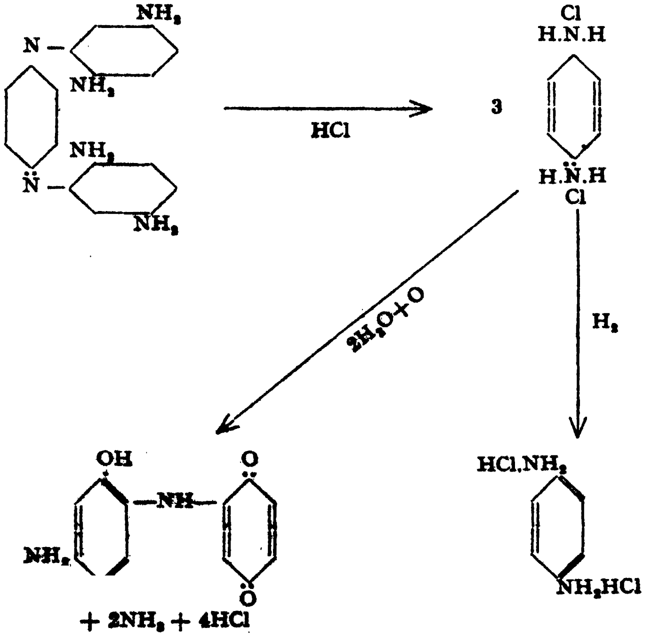
(2)



There is here no red compound and no ammonia; these are the products of the main reaction. The yield of para-phenylenediamine in the main reaction corresponds with about two-fifths of the base used, and the ammonia with one other molecule of para-phenylenediamine decomposed. Thus, it seems certain that two molecules of the diamine remain in the black compound which, we think, has the structure of a quinonoid derivative of para-phenylenediamine—possibly polymerised. The formation of this compound probably results in the following manner:



(3)



If these views are correct, there is the curious anomaly of oxidation and reduction proceeding simultaneously. The red compound is, presumably, the hydrochloride of quinone diimine which was described by Willstätter and Mayer,[10] as forming a violet-coloured solution, but which cannot be isolated. This action of hydrogen chloride is not without precedent, though we suggest it is most unusual for such stable groupings as quinone rings to be split in this way.

On the basis of the equation (3) it may be calculated that 5 g. of the Bandrowski base should yield 3·6 g. of black compound with 0·53 g. of ammonia and 1·68 g. of para-phenylenediamine. Comparison of these figures with the actual yields obtained shows that the black compound and ammonia formed are somewhat below the theoretical quantities, and the para-phenylenediamine somewhat higher. These facts point to concurrence of reaction (2), so that we think that these two equations correctly explain what happens and represent the constitution of the two interesting products.

In view of the analytical importance of differentiating between the red colour produced from logwood and that of the decomposition product of Bandrowski base, it may be useful to record the reactions of these substances and of the oxidation product of para-aminodimethylaniline, which breaks down similarly. Furs dyed with this compound present many similarities to those dyed with simple para-phenylenediamine. No difficulty arises in the identification of logwood by the familiar reactions with alkalis and with alum, but the following reactions may be found useful when the presence of an oxidation product of an amine is suspected.

Reduce the red liquid with zinc dust, filter, make the solution nearly neutral with chalk, and then apply the indamine reaction. Logwood gives no colour other than a dirty brown; para-phenylenediamine from Bandrowski base gives a green or blue according to the quantity; para-amino-dimethylaniline gives a pink or green colour according to quantity. The latter compound may be further identified by the intense crimson—Wurster's red—which it gives on the careful addition of very weak bromine water; the slightest excess of bromine discharges the red colour, leaving only the logwood. Logwood is reduced with difficulty by sodium formaldehyde sulphoxylate, whereas furs dyed with amino compounds are reduced fairly readily. Sodium hypochlorite bleaches logwood colour or that of the oxidised diamines, but the latter give a slight precipitate of the chloroimines, the melting-point of which serves to identify the amino compound, if sufficient can be separated.

SUMMARY.—A study has been made of the decomposition of Bandrowski's base by boiling it with dilute hydrochloric acid. The intermediate product has a strong violet-red colour resembling logwood extract, and is probably an unstable quinonediimine dihydrochloride. The final products are para-phenylenediamine and a black quinonoid compound, $C_{12}H_{10}N_2O_2$ (for which a structural formula is given), together with small amounts of carbon dioxide and hydrogen cyanide. The mechanism of the reactions is discussed. Notes are given of the analytical reactions by which the red products of decomposition of Bandrowski's base and its analogues prepared from di-methyl-*p*-phenylenediamine may be detected in the

presence of logwood—a problem arising in logwood-dyed furs which have been topped by means of a diamine.

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DISCUSSION

Mr. C. E. SAGE said that Dr. Cox had proceeded a step further along the road, and some present had been able to follow him in the various steps. The present one was important from a commercial point of view, because one did get furs which were not only dyed but also treated—or, to use the technical term, "topped"—and it was at times difficult to determine whether or not the topping had anything to do with the dermatitis. He asked Dr. Cox if he thought that Bandrowski's base was definitely the cause of any skin trouble, since this was a point which often had to be considered in dealing with supposed cases of dermatitis.

Dr. H. E. Cox, replying, said that, in his opinion, Bandrowski's base itself was a harmless substance, but the important and sometimes difficult point to establish was first of all whether the logwood-dyed fur had been topped at all, and if it had, whether there was any imperfectly oxidised diamine left in or on it. He often heard suggestions that various substances were irritant, but thought that it ought to be incumbent upon a person making such allegation to demonstrate that the substance suspected and no other was present, and that it was really the cause of the dermatitis. It was generally so easy to make accusations against either persons or substances, sometimes on inadequate grounds, and very difficult to refute such suggestions.

Vitamin Potency and Associated Characteristics of Average Cod-Liver Oil

BY RONALD SYDNEY MORGAN, B.Sc., A.R.C.S.,
AND HARRY PRITCHARD, B.Sc.

(*Read at the Meeting, February* 6, 1935)

THOUGH manufacturers of concentrated preparations of vitamins *A* or *D* generally state that their products are so many times more potent than cod-liver oil, there are no satisfactory published figures giving the vitamin potency of average medicinal cod-liver oil. In the B.P. Codex, 1934, it is stated (p. 720) that the average blue value of cod-liver oil is 15, and that the range is 6 to 50, and (p. 721) that an average sample of cod-liver oil contains about 2000 units of vitamin *A* and 100 units of vitamin *D* per gram. No reference, however, is made to the work on which these figures are based.

The pass blue value of cod-liver oil in the 1932 British Pharmacopoeia is 6, and the pass biological values recently adopted by the United States Pharmacopoeia Commission,[1] which came into force on 1st January, 1935, are 600 international units of vitamin *A* and 85 international units of vitamin *D* per gram.

The average blue value of 38 samples of cod-liver oil, purchased retail, was determined in this laboratory in 1927. The technique of the determination has been modified since then, chiefly in the substitution of a 10-mm. cell for an 8-mm. tube, but the figure obtained should correspond to a blue value, as now defined, of 8·0. The present work was undertaken in order to repeat the determination of the average blue value, and to obtain values for the vitamin-*A* potency and vitamin-*D* potency of medicinal cod-liver oil as purchased retail; for this purpose, bottles of cod-liver oil were purchased from retail chemists in various parts of the British Isles in November, 1933.

Blue Value.—The determination of blue values followed the technique described in the British Pharmacopoeia, 1932, and a certain number of blue values *via* the unsaponifiable matter were determined. For the determination *via* the unsaponifiable matter, this was extracted from the cod-liver oil by the following method:

From 2 to 2·5 g. of the oil are saponified with 20 ml. of approximately 2 *N* alcoholic potash, by heating on a water-bath for 3 to 5 minutes, with continual agitation. Fifty ml. of ether are added to the mixture before it is quite cold, and the whole is poured into a separating funnel. The saponification flask is washed out with 100 ml. of water, which are added to the liquid in the separating funnel. The funnel is rotated and separation takes place. The soapy layer is removed and washed once with 50 ml. of ether. The extracts are combined, washed 3 times with about 25 ml. of water at each washing, and evaporated in a current of carbon dioxide or nitrogen. The residue is freed from water by adding alcohol and evaporating, and is then dissolved in chloroform.

This method gives results comparable with those obtained by following the Society of Public Analysts' method for the determination of the unsaponifiable matter in fats and oils.[2] The present technique was adopted to facilitate rapid extraction of the unsaponifiable matter. To avoid loss of blue value, the unsaponifiable matter should not be left standing long in ethereal solution unless peroxide-free ether is used.

All the following results are grouped in a frequency diagram in Fig. 1 (p. 358). Of the 67 samples whose direct blue values were determined, 48 gave values below the average, and 19 gave values above, while of the 36 samples whose blue values *via* the unsaponifiable matter were determined, 24 gave values below the average, and 12 gave values above. The average direct blue value of the 67 samples was 7·8, and the median value 6·5; the average blue value *via* the unsaponifiable matter of the 36 samples was 27, and the median value was 22·8.

The district group averages of the direct blue values varied from 7 to 9·3, with a general average of 7·8. The blue values of 24 per cent. of the samples were lower than the British Pharmacopoeia pass value of 6, but it is doubtful whether much significance can be attached to this, since it was found difficult to obtain

TABLE I

BLUE VALUES OF SAMPLES OF COD-LIVER OIL PURCHASED RETAIL

Group (i) Samples from Lancashire, The Wirral and Yorkshire.
„ (ii) „ „ Lincolnshire, Staffordshire, Warwickshire and Northamptonshire.
„ (iii) „ „ London and district.
„ (iv) „ „ Hampshire, Somerset, Dorset and Devon.
„ (v) „ „ Scotland and Ireland.

Group (i)

Blue value	Blue value *via* unsaponifiable matter
5·0	19·6
5·4	25·9
6·0	—
6·2	21·9
6·6	20·0
6·8	—
6·9	15·6
7·1	32·8
7·2	—
7·8	23·1
7·8	—
8·1	—
8·5	28·4
11·6	—
15·2	41·6

Average for Group (i)

7·75	25·4

Group (ii)

Blue value	Blue value *via* unsaponifiable matter
3·5	22·2
4·1	19·4
5·7	—
6·3	—
6·4	23·6
7·3	—
7·3	—
7·6	—
7·9	—
8·1	—
8·1	—
13·2	40·8
15·0	36·7
19·4	41·7
20·0	40·5

Average for Group (ii)

9·3	32·1

Group (iii)

Blue value	Blue value *via* unsaponifiable matter
4·8	—
4·9	23·5
4·9	—
5·7	20·2
5·8	—
6·2	21·1
6·9	19·3
6·9	25·8
7·0	19·8
7·0	—
7·7	19·2
7·9	19·5
10·0	37·0
13·2	42·1
13·8	46·5

Average for Group (iii)

7·5	26·7

Group (iv)

Blue value	Blue value *via* unsaponifiable matter
3·5	19·0
5·5	—
5·5	—
5·7	—
6·5	—
6·5	—
6·5	—
6·6	20·1
6·7	25·1
7·0	—
7·4	—
16·0	—

Average for Group (iv)

6·95	21·4

Group (v)

Blue value	Blue value *via* unsaponifiable matter
5·5	19·2
5·7	—
6·1	22·0
6·5	18·1
6·5	31·0
6·6	—
6·8	—
7·4	—
8·5	22·5
11·8	47·2
Average for Group (v)	
7·1	26·7

GENERAL AVERAGES

Blue value	Blue value *via* unsaponifiable matter
7·8	27·0
(67 samples)	(36 samples) (Blue value of these 36 samples = 8·4.)

satisfactory duplication of results in the determination of the blue value of an oil of low blue value, because of the abnormal rapidity of fading usually observed. Of the 16 samples with blue values less than 6, 13 had blue values about 4·5, and the blue values of any of these might be recorded in other laboratories as 6. The average value of the ratio (blue value *via* unsaponifiable matter)/(direct blue value) is 3·5; this is unexpectedly high. Dyer[3] published the results of the examination of 30 samples of oil by the two methods; the direct blue values varied from 4·4 to 86 with an average of 24·4, and the average ratio (blue value *via* unsaponifiable matter)/(direct blue value) was 1·615. Dyer's highest value was 2·055, whilst the lowest value in the present series was 2·03. The large difference between the average ratio recorded by Dyer and that now found may be due to two causes:—(i) Dyer was not dealing with oils purchased retail, and the average blue value was much higher than in the present series, so that it would be expected that the direct test would be less interfered with by inhibition, and (ii) Dyer used chloroform to extract the unsaponifiable matter, whilst ether was used in the present tests; ether is recommended for the efficient extraction of unsaponifiable matter from fish oils, and chloroform is known to exert a destructive action on vitamin *A*.

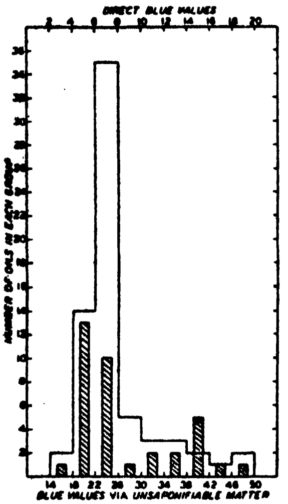

FIG. 1.

Distribution of 67 cod-liver oils according to direct blue value (open figure) and of 36, from the same series, according to blue value *via* the unsaponifiable matter (shaded columns).

Composite samples of the cod-liver oils were prepared for biological assay from 64 samples. Three others, included in Table I, were received later; these had an average blue value of 10, so that their inclusion in the composite samples would not have significantly affected the results. The 64 bottles of oil were from 10 ml. of each of the samples below median and from 10 ml. of each of the samples above median. Later a composite sample of all the 64 samples was prepared from 25 ml. of each. Determination of the blue values gave the following results (Table II):

TABLE II

BLUE VALUES OF COMPOSITE SAMPLES PREPARED FROM 64 SAMPLES OF MEDICINAL COD-LIVER OIL

	Blue value	Blue value *via* unsaponifiable matter
Oil I (samples below median)	7·5	19·1
Oil II (samples above median)	10·5	24·4
Averages ..	9·0	21·6
Oil III (mixture of Oils I and II ..	9·6	20·6
Oil IV (64 samples re-bulked)	9·4	23·2
Average of last three values ..	9·3	21·8

The best values for average cod-liver oil are, therefore:

Direct blue value .. .. 9·3

Blue value *via* unsaponifiable matter .. 21·8

It is not surprising that the blue value of the average oil (= 9·3) does not agree with the average blue value of the individual oils (= 7·8), since the blue value is affected so much by inhibition. The blue value *via* the unsaponifiable matter of the average oil (= 21·8) is less than the average blue value *via* the unsaponifiable matter of the 36 oils examined separately (= 27). This may be explained partly by an unequal distribution of oils of high blue value in the sample of 36 oils and the whole series (the average direct blue value of the 36 oils was 8·4, while the average for the whole series was 7·8), and partly by the errors inherent in the test.

SPECTROPHOTOMETRIC EXAMINATION.—We are indebted to Dr. R. A. Morton, of Liverpool University, for making these examinations. The results are as follows:

	Oil I (Oils below median)	Oil II (Oils above median)	Oil III (Average cod-liver oil)
Extinction coefficient (1 per cent. solution in 1 cm. cell) at $328 m\mu$, on oil	0·50	0·70	0·575
Extinction coefficient (1 per cent. solution in 1 cm. cell) at $328 m\mu$, *via* unsap.	0·45	0·55	0·51
Percentage of vitamin *A* of extinction coefficient = 1600	0·028	0·034	0·032

Extinction coefficients at $328 m\mu$ of cod-liver oils determined *via* the unsaponifiable matter are invariably lower than those determined directly on the oils, presumably because of the removal of inactive absorbing substances in the soap.

The best values for average cod-liver oil have been calculated from the result on Oil III and the average of the results on Oils I and II as

$$E^{1\%}_{1\,\mathrm{cm.}}\ 328m\mu, \text{ on oil}, = 0{\cdot}587$$
$$\text{,,} \quad \textit{via} \text{ unsap.} = 0{\cdot}505$$
$$\text{Per cent. of vitamin } A = 0{\cdot}0315$$

DETERMINATION OF VITAMIN *A* BY BIOLOGICAL ASSAY.—The assays were made according to our standard technique.[4] Assays were made of the vitamin-*A* content of the Oils I and II, and, when these were completed, of Oil IV (re-bulk of all samples).

Oils I and II.—Doses were chosen on the expectation of about 350 units per g. in Oil I and about 450 units per g. in Oil II. Rats were selected in triads, one of each triad receiving a daily dose of the international carotene standard, another a daily dose of Oil I, and the third a daily dose of Oil II. The rats of any triad were of the same litter and the same sex, as nearly as possible equal in weight at the beginning of test, and the tests on all were started the same day. At the end of the test, there were 9 pairs of bucks and 10 pairs of does available for comparison of Oil I and the standard, and 10 pairs of bucks and 8 pairs of does for comparison of Oil II and the standard. The growth given by the doses of the oils generally exceeded that given by the comparative doses of standard, and from the average differences in the squares of the growth the assays were calculated as:

Oil I (samples below median blue value): 530 units per g.
Oil II (,, above ,, ,, ,,): 798 ,, ,,
Average : 664 ,, ,,

Oil IV.—For the assay of Oil IV (the average sample of the 64 oils), doses were chosen on the expectation of 650 units per g., as indicated by the average of the values found for Oils I and II. All the animals were bucks, and 13 pairs were used for the assay. From the average difference in the squares of the growth, the assay was calculated as 673 units per g. This value agrees almost exactly with the average of the assays of Oils I and II, *viz.* 664 units per g., and the assay may, therefore, be accepted as 670 units per g.

Error of the Result.—The separate assays of Oils I and II employed, respectively, 9 pairs of bucks and 10 pairs of does, and 10 pairs of bucks and 8 pairs of does. Since about twice as many pairs of does as of bucks are required for assays of equal accuracy,[5, 4] the assays may be regarded as each employing 14 pairs of bucks; and, since the controls receiving the carotene standard were the same in both assays, the average of the results of Oils I and II may be regarded as a single assay employing $14 \times \frac{3}{2} = 21$ pairs of bucks. Thirteen pairs of bucks were used in the assay of Oil IV, and thus the final average value of 670 units per g. may be regarded as representing the average of the results from 34 pairs of bucks. From the data given in the paper describing the technique of the test[4] it is calculated that in an assay employing 34 pairs of bucks, there is a 22/1 chance that the error does not exceed −14 or +17 per cent., and an 8/1 chance that it does not exceed 8 per cent. From the variation within the particular tests under consideration, assuming the relation between growth response and dosage given in the paper, the errors calculated are -11 or $+12$ per cent. for a 22/1 chance, and 6 per cent. for an 8/1 chance.

Determination of Vitamin *D* by Biological Assay.—The assays were made according to our standard technique.[6] Assays were made of the vitamin-*D* content of Oils I and II, Oil III and Oil IV.

Oils I and II.—Doses were chosen on the expectation of 100 units per g. in each oil. The rats were selected in triads in the same way, one of each triad receiving a daily dose of the international vitamin-*D* standard, another a daily dose of Oil I, and the third a daily dose of Oil II. After 10 doses had been given to each, the rats were killed, and the radii and ulnae were dissected out, sectioned, and stained with silver nitrate. Camera-lucida drawings of the sections were made (magnified 11 diameters), and the healing was assessed as the area of the "line" in square mm. Seven triads were used, and the assays were calculated from the average differences in the healing produced by the standard and the oils as:

Oil I (samples below median blue value): 52·5 units per g.
Oil II (,, above ,, ,, ,,): 85·5 ,, ,,
Average : 69 ,, ,,

Oils III and IV.—For the assay of Oil III doses were chosen on the expectation of 70 units per g., as indicated by the average of the assays of Oils I and II; 16½ pairs were used, and the assay was calculated as 90 units per g. Oil IV, a re-bulk of the original 64 samples, should be identical with Oil III. It was fed at the same levels of dosage, 13½ pairs of rats were used, and the assay was calculated as 78 units per g. If the two assays are considered as one with 30 pairs of rats, the assay is 84·2 units per g. This value is rather higher than the average of the assays of Oils I and II, *viz.* 69 units per g. In calculating the general average, the 7 triads of the assays of Oils I and II may be weighted as 7 × 1½ pairs. The total number of pairs then becomes 40, and the final average 81 units per g.

Error of the Result.—From the data given in the paper on the technique of the test[6] the error expected in an assay with 40 pairs of rats is calculated as -11 or $+12$ per cent. for a 22/1 chance, or 6 per cent. for an 8/1 chance. From the variation within the actual tests the error is calculated as -14 or $+16$ per cent. for a 22/1 chance, or 8 per cent. for an 8/1 chance.

Discussion.—The characteristics of average cod-liver oil as determined in the work here reported are:

Blue value : 9·3
Blue value *via* unsaponifiable matter: 21·8
$E^{1\%}_{1\,\mathrm{cm.}}$ $328m\mu$: 0·505
Biological assay for vitamin *A* : 670 units per g.
,, ,, ,, ,, *D* : 81 ,, ,,

The richest concentrate of vitamin *A* prepared by Carr and Jewell[7] had $E^{1\%}_{1\,\mathrm{cm.}} = 1600$, a blue value of 78,000, and a biological assay of about 1·67 million units per g. From the data given above, it would be calculated that a vitamin-*A* preparation with an extinction coefficient of 1600 should have a blue value of 69,000 and a biological assay of 2·12 million units per g. From other assays of liver oils and concentrates, to be reported in another paper, however, it appears that the ratio of biological assay to extinction coefficient at $328 m\mu$, or to blue value, is rather higher for cod-liver oils than it is for richer sources of vitamin *A*.

The values are throughout lower than those given in the B.P. Codex 1934 of 2000 units of vitamin *A* and 100 units of vitamin *D* per g., and blue value = 15. The difference is particularly striking in the case of the biological assay of vitamin *A*, but the difference in blue value is considerable; only 5 of the 67 samples purchased reached or exceeded a blue value of 15.

It is of interest to note that the potency of average medicinal cod-liver oil, as purchased retail in the British Isles, is of the same order as the pass value recently published by the U.S. Pharmacopoeia Commission,[1] *viz.* 600 units of vitamin *A* and 85 units of vitamin *D* per g.

SUMMARY.—The vitamin potencies of an average sample of cod-liver oil prepared by mixing together equal quantities of 64 samples of medicinal cod-liver oil, purchased retail from pharmacies in various parts of the British Isles, were determined as:

670 international units of vitamin *A* per g.
81 „ „ „ „ *D* „

These assays were based on results from about 40 pairs of rats in each assay. It is calculated that there is a 22/1 chance that the error of the vitamin-*A* assay does not exceed −14 or +17 per cent., and that the error of the vitamin-*D* assay does not exceed −14 or +16 per cent.

The characteristics associated with vitamin *A* of the average oil were:

Blue value	: 9·3
Blue value *via* unsaponifiable matter	: 21·8
Extinction coefficient at $328 m\mu$ (1 per cent. solution in a 1 cm. cell) *via* unsaponifiable matter	: 0·505

APPENDIX

Details of the growth obtained in the vitamin-*A* assays and of the healing obtained in the vitamin-*D* assays are given below:

TABLE III

VITAMIN-*A* ASSAY OF OILS I (BELOW MEDIAN BLUE VALUE) AND II (ABOVE MEDIAN BLUE VALUE).

(Growth is expressed as the average of the growths made in 4 weeks, 5 weeks and 6 weeks)

		Standard		Oil I			Oil II		
		Growth in g.			Growth in g.			Growth in g.	
Litter	Dose Units	Bucks	Does	Dose Mg.	Bucks	Does	Dose Mg.	Bucks	Does
820	¾		16	2·14		43·3	1·66		—
	1		54·7	2·86		41	2·22		—
822	½	14·7		1·43	39		1·11	46	
824	1		43	2·86		39·7	2·22		37
	2	88·3		5·72	95·3		4·44	97	
826	¾		23·7	2·14		45·3	1·66		—
	1	57·7		2·86	49		2·22	73·3	
828	¾		21	2·14		—	1·66		40
830	1		47·3	2·86		56	2·22		59
	2	81·7		5·72	88·3		4·44	89·3	
832	½		22·7	1·43		34·7	1·11		35·3
	1	67·3		2·86	84·3		2·22	88	
	2	92·3		5·72	102·3		4·44	102	
834	1		30	2·86		64·7	2·22		57
839	1	34·3		2·86	63·3		2·22	79·7	
	2	56·3		5·72	77·7		4·44	84	
841	¾		43·3	2·14		58·7	1·66		59·7
	1		57·7	2·86		67	2·22		67
843	¾		42·7	2·14		46	1·66		57·7
	1	63		2·86	80		2·22	75	
	2	82		5·72	—		4·44	100·3	

From these figures, the potencies of the oils are calculated from the relations:

The square of the growth

$$= C_1 + 10730 \log \text{dose (bucks)}$$
$$= C_2 + 4350 \log \text{dose (does)}.$$

The values obtained are:

Oil I (samples below median blue value): 530 units per g.
Oil II („ above „ „ „): 798 „ „
Weighted average : 664 „ „

TABLE IV

VITAMIN-*A* ASSAY OF OIL IV (AVERAGE SAMPLE OF 64 OILS)

(Bucks only were used in this Assay)

	Standard			Oil IV		
Litter	Dose Units	Growth in 3 weeks	Growth averaged at 4, 5 and 6 weeks	Dose Mg.	Growth in 3 weeks	Growth averaged at 4, 5 and 6 weeks
906	2	55	76·3	3·08	40	71
		48	61·7			
907	1	41	61·3	1·54	35	54
908	1	28	46·7	1·54	35	61
909	¾	24	35·7	1·15	32	50·7
910	1	45	67·7	1·54	51	68
	1	44	66			
911	1	34	41·3	1·54	34	43·4
912	¾	40	64	1·15	49	70·7
960	1	54		1·54	39·3	
	2	73·6		3·08	61·6	
965	2	53·3		3·08	61·3	
969	¾	52·7		1·15	47·7	
970	1	26·4		1·54	51·3	

The assay from the 4, 5, 6-week experiments is 719 units per g., and the assay from all the 3-week values, calculated from the relation:

the square of the growth = C + 5930 log dose (bucks), is 650 units per g. The weighted average of the assays, allowing for the difference in accuracy of 3-week and 4, 5, 6-week experiments, is 673 units per g.

TABLE V

VITAMIN-*D* ASSAY OF OILS I (BELOW MEDIAN BLUE VALUE) AND II (ABOVE MEDIAN BLUE VALUE)

(Healing is measured as the area in sq.mm. of the "line" in the 11 × magnified drawing of radius and ulna)

	Standard		Oil I		Oil II	
Litter	Dose Units	Healing Sq.mm.	Dose Mg.	Healing Sq.mm.	Dose Mg.	Healing Sq.mm.
833	⅛	132	1·25	68	1·25	80
	¼	156	2·5	84	2·5	160
	½	210	5	183	5	230
836	¼	58	2·5	60	2·5	72
	½	122	5	68	5	106
838	¼	150	2·5	58	2·5	146
	½	162	5	116	5	110

The assays are calculated from the relation:

$$\text{Healing} \doteq C + 180 \log \text{dose}$$

as

Oil I	52·5 units per g.
Oil II	85·5 „ „
Average	69 „ „

TABLE VI

VITAMIN-*D* ASSAY OF OIL III (MIXTURE OF OILS I AND II)

	Standard		Oil III	
Litter	Dose Units	Healing Sq.mm.	Dose Mg.	Healing Sq.mm.
860	¼	44	3·57	90
864	¼	180	3·57	210
866	¼	79	3·57	115
868	⅛	21	1·79	74
	¼	110	3·57	63
	½	95	7·15	93
870	⅛	34	1·79	55
	¼	100	3·57	73
	½	174	—	—
872	¼	108	3·57	99
	½	166	7·15	228
884	¼	130	3·57	152
	½	194	7·15	210
889	¼	133	3·57	60
	½	182	7·15	196
891	¼	50	3·57	160
	¼	86	3·57	184

The assay is calculated as: Oil III = 90 units per g.

TABLE VII

VITAMIN-*D* ASSAY OF OIL IV (AVERAGE SAMPLE OF 64 OILS)

	Standard		Oil IV	
Litter	Dose Units	Healing Sq.mm.	Dose Mg.	Healing Sq.mm.
915	⅛	29	1·79	50
	¼	106	3·57	103
916	½	108	7·15	106
917	¼	92	3·57	64
918	½	122	7·15	107
919	¼	52	3·57	84
	½	106	7·15	104
934	¼	62	3·57	125
			3·57	80
	½	126	7·15	92
938	¼	48	3·57	77
939	¼	76	3·57	86
940	½	112	7·15	138
941	½	105	7·15	120

The assay is calculated as: Oil IV = 78 units per g.

The separate vitamin-*D* assays are as follows:

Oil I	52·5	units per g.
Oil II	85·5	,, ,,
Average	69	,, ,,
Oil III	90	,, ,,
Oil IV	78	,, ,,
Weighted average of last 3 values	81	,, ,,

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DISCUSSION

Dr. K. H. COWARD said that her own experience was not exactly comparable with that of the authors. The samples that she had examined had come direct from manufacturers and were, presumably, quite fresh specimens. However, it might interest them to know the kind of values she had obtained.

Some twenty-four samples examined individually during the past five or six years had an average of 2200 units of vitamin *A* per gram, which was considerably higher than the authors' figures. The actual values found varied between 500 and 8400 units. The values for vitamin *D* ranged from 40 (one sample had given 20) to about 360; the average of 208 samples of cod-liver oil which she had assayed came to 167 units, double the figure given in the paper. This raised one or two points of interest. The oils with which she had had to deal were, presumably, freshly prepared. Secondly, they would notice that she had examined far more samples for vitamin *D* than for vitamin *A*, which probably indicated that producers were relying on the "blue value" or the *E* value, as a measure of the vitamin *A* value of an oil. This blue value certainly had its use, and the spectroscopic method was more valuable. Another point which influenced the kind of samples and the number of samples examined was the fact that poultry breeders and makers of cattle food were impressed by the necessity of giving animals vitamin *D*. Moreover, the number of samples of oils she had had for poultry feeding far exceeded the number of medicinal oils. Of course, she was not always told for what the oils were intended, or the source of the oils—in fact she was not told very much about them at all. The point that emerged from comparison of the figures was that her oils were richer in vitamin *D* than those of the authors; hence, did cod-liver oil lose vitamin *D* on keeping? Sometimes the oils were kept for a year or two in pharmacists' shops. She was experimenting on this question at the present time, but naturally it was an experiment that took some time to complete. The other question was: Were oils prepared for medicinal purposes really inferior in vitamin *D* content to oils prepared for poultry feeding?

Mr. N. EVERS remarked that what puzzled him was how Mr. Morgan had obtained such inferior samples of cod-liver oil. He, himself, had had quite a lot to do with all sorts of cod-liver oil, and he had hardly ever come across oils of such low values as Mr. Morgan's. Whether there was any deterioration in the pharmacists' shops, he was not prepared to say, but his own samples did not show deterioration in a reasonable time, and it really puzzled him very much, unless they had been kept in the sunlight in a window for some time, which was the only factor he knew that caused serious deterioration in cod-liver oil.

Mr. A. L. BACHARACH emphasised the agreement, now practically unanimous, that the blue test on an oil would give something approaching a quantitative estimate of its vitamin *A* content only if it was carried out on the unsaponifiable matter. Even so, quite marked differences could be obtained by different observers. The same individual, working with the test in the same laboratory, using the same apparatus and the same source of light, could obtain very good duplicates, but with different apparatus the agreement might be less satisfactory. Two different individuals, even working with the same apparatus and illumination in the same laboratory, might get results sufficiently different to justify their being called as experts on opposite sides in a court case. He was not, however, satisfied that the differences obtained were wholly due to personal factors and errors of manipulation.

It had been shown by various workers that absolutely fresh oil, kept out of contact with air, had an extremely low blue value, which increased on keeping, and could be augmented artificially by various means, such as by passing ozone through it. It had been suggested that the inhibiting substances originally present suppressed the blue colour, but were themselves destroyed by oxidation. On the other hand, many investigators had reported a slow diminution in blue colour in ordinary pharmaceutical oils when they were kept under quite good conditions of storage. It was not impossible to reconcile these observations. Nothing was known about the chemical nature of inhibitors occurring naturally in cod-liver oil. It was conceivable that these inhibitors were destroyed or otherwise put out of action by ozone, but that they might actually increase under the ordinary conditions of storage in the pharmacist's shop and elsewhere. Theoretically, indeed, it was possible that the relatively low results obtained by Mr. Morgan for the direct blue values were due to gradual accumulation of inhibiting substances.

He would like to ask the authors whether they had grouped their samples so as to show which of them bore the brand names of reputable firms who were in a position themselves to assay them biologically or to have such assays carried out. If the number of "nameless" brands of oils sold throughout the country were high, the results were fairly easily explained, for the ordinary pharmacist obtaining his cod-liver oil at the lowest possible price from any convenient distributor would be very unlikely to get biologically assayed oil.

Mr. H. JEPHCOTT suggested the possibility of some relation between the facts that cod-liver oil was a semi-drying oil and that the inhibiting factors increased on keeping.

Dr. E. LESTER SMITH said that he wished to refer to the question of determining blue values on the unsaponifiable matter. He agreed with Mr. Morgan that ether was preferable to chloroform for extracting the soap solutions. As part originator of the technique which had become known as "the Smith-Hazley method," he would say that they had been for some time suspicious of the test, particularly when they came to examine rich oils, such as halibut-liver oils, and got lower blue values on the unsaponifiable fractions than on the oils. Lately they had been following the vitamin *A* spectroscopically, and had found that there was definite risk of partial destruction when chloroform was used for extraction. In view of this, it was not surprising that Mr. Morgan obtained higher results than Dyer for the average ratio of the blue value on the unsaponifiable fraction to the direct blue value, since Dyer used chloroform. Nevertheless, he was surprised at the magnitude of the average ratio—3:5; in his experience, only very stale oils had shown such a high ratio.

Dr. F. H. CARR complimented the authors on their admirably presented paper. He, like others, was surprised at the low Carr-Price blue values obtained by the authors on the original oils. His firm, as manufacturers and wholesalers, had examined, over many years, large numbers of all kinds of liver oils, but these, of course, were always fresh and had not been held in stock in pharmacists' shops. In his experience, blue values lower than 10 were rare; on the whole, the average was more like 18. After hydrolysis, however, the figures given by Mr. Morgan were similar to those which he had observed. Notwithstanding Dr. Lester Smith's remarks, he would still regard the chloroform method as workable if proper precautions were taken.

Dr. D. C. GARRATT said that he thought he could supply a connecting link between the statements of Dr. Carr and Mr. Morgan, as he had analysed many samples in the laboratories of the London County Council, which obtained large supplies of both cod-liver oil and extract of malt with cod-liver oil direct from reputable wholesalers. Therefore he could give a very good idea as to the quality of oil the retail pharmacist should receive; 9·3 seemed to him to be a low value. He found 12 to 14 was a very good average. If there were some loss of vitamin on storage, it could not be great.

Mrs. K. LATHBURY remarked that the ratio of biological test to colour test to spectrophotometric test ought to be interesting. She had worked out the averages of her figures and found that this ratio was 130 : 27 : 1, and Mr. Morgan's corresponding figures were 141 : 37 : 1. In other words, they appeared to agree in the biological and spectrophotometric tests, but not in the colour test on the unsaponifiable matter. If she applied the ratio obtained from the average of her results to Mr. Morgan's figures, she got 565 instead of 530, 791 instead of 798, and 650 instead of 670. The agreement between the biological and spectrophotometric tests was good, but they had to find out what had happened in the colour test.

Mr. E. HINKS remarked that from time to time he had had occasion to examine the blue value, and 9 was quite a high figure. He often got 6 or 7, but these were with retail samples.

Mr. MORGAN, replying, suggested that not only were the oils examined by Dr. Coward not comparable with those examined in the present work, but that they might not be fairly representative of fresh oils, since oils submitted to the Pharmaceutical Society for assay might be oils in which the manufacturers were especially interested. He knew it was possible to obtain cod-liver oils of high blue value and vitamin-*D* potency, but there was sometimes a suspicion that exceptionally potent oils were not genuine cod-liver oils. The purpose of the present work was to determine the average potency of cod-liver oil as sold retail; the oils were obtained through commercial travellers, who purchased bottles of cod-liver oil, as ordinary customers, at various pharmacists' shops in their districts. Details of the labels had been recorded. Most of the samples were labelled simply "Cod-liver Oil," with the retail pharmacist's name. The branded samples were in a minority, and he did not remember what the particular figures for these were. In the determination of blue values *via* unsaponifiable matter, he had never used chloroform, except in a few early experiments, because he had found that chlorsolvents generally produced destruction of vitamin *A* when heated with concentrates. The high ratio of unsaponifiable matter to direct blue value was partly due to the inclusion of several oils of very low direct blue value. He thought that the agreement between the average blue value *via* unsaponifiable matter given in the paper and Dr. Carr's estimate might be illusory; the direct blue value of a certain cod-liver oil, "Oil Z," had been determined in three laboratories (Dr. Coward's, Mr. Morgan's, Dr. Carr's) as 12, 13 and 12, respectively, but the agreement in the determinations *via* the unsaponifiable matter was much less satisfactory, Mr. Morgan's value being 33, and the other laboratories' values about 25. He thought that Mr. Jephcott's suggestion might afford an explanation.

The Detection of Japanese Mint Oil in Peppermint Oils

By D. C. GARRATT, B.Sc., Ph.D., F.I.C.

(*Read at the Meeting, April* 3, 1935)

ADULTERATION of peppermint oil has undoubtedly been widely practised by substitution of inferior for higher grades, and the close resemblance between the constants, both physical and chemical, of oils from the various species of plant renders detection difficult.

As Japanese oil (from *Mentha arvensis*) is not recognised by the British Pharmacopoeia, a colour test is included to distinguish this oil from the other better varieties (from *Mentha piperita*). This is one of the numerous colour reactions which have been devised for this purpose (Umney, *Perf. & Ess. Oil Record*, 1910, **1**, 298; 1911, **2**, 275; Eaton, *J.A.O.A.C.*, 1922, **5**, 597), but they all suffer from the defect that they are positive for genuine oils from *Mentha piperita*, and negative for the cheapest oil (Japanese); hence gross adulteration with this may be practised, and yet the product will still give the characteristic reaction for the better quality oil.

At present the analyst has to rely mainly on odour and taste, especially the latter, but, except to the expert, these are uncertain means of detecting small additions of Japanese oil.

In the course of an investigation with large quantities of the low-boiling fractions of Japanese oil, furfuraldehyde was detected. It was estimated in this particular case as being present to the extent of 0·018 per cent., calculated on the original oil. This proportion of furfuraldehyde was found to be sufficient to give a typical aniline acetate colour reaction. When the test was applied to American oil, a slight colour developed, but to a much smaller degree. It was felt that even the least assistance in the difficult task of the evaluation of peppermint oils would be welcomed, and this colour difference promised to be a possible aid in the problem. With this object in view, the following investigation was carried out, the results being sufficiently encouraging for the method to be offered as a tentative test.

Some oils gave trouble, because the deep yellow colour developed with the reagent was sufficient to mask or influence any red colour produced. This objection was overcome by using small quantities of oil and adopting the tintometer for measuring the colour values, these being taken after intervals of 5, 10, 15, and 30 minutes.

After data had been compiled from many samples, the most suitable figure to be taken for comparison was found to be that of the colour given after 10 minutes' contact between the oil and the reagent.

The details of the test as finally standardised, are as follows:—The oil (0·1 ml.), measured from a 1-ml. pipette (graduated in 1-100th of a ml.), is mixed in a test-tube with 5·0 ml. of a 2 per cent. solution of freshly redistilled aniline in glacial acetic acid, added from a burette. The reaction mixture is examined in a 1-cm. cell of a Lovibond tintometer (B.D.H. pattern) after an interval of 10 minutes. The reaction mixture must be protected from bright light. As this fact was not realised until later, many experiments had to be repeated.

Many samples of American oil, some authentic and others branded specimens, direct shipments from the U.S.A., which, if adulterated, could only have been sophisticated in that country, were subjected to the test. Table I shows the results obtained. For simplicity, only red values are recorded, except with the first five samples, which illustrate the typical range of yellow values developed.

TABLE I

AMERICAN OILS

Index No.	Brand			Tintometer value					
				10 minutes		15 minutes		30 minutes	
				Y	R	Y	R	Y	R
1	Todd, Feb. 1932	2·0	0·5	2·3	0·7	2·4	0·7	4·3	1·7
2	,, May, 1932	0·7	0·4	0·7	0·5	0·8	0·6	1·4	0·8
3	,, extra Jan. 1933	1·7	0·5	1·8	0·6	1·9	0·7	3·1	1·0
4	,, fair Jan. 1933	0·9	0·6	0·9	0·6	1·3	0·7	1·6	1·0
5	,, June, 1934	0·8	0·5	0·8	0·7	0·9	0·7	1·5	1·1
6	,, Aug. 1934		0·4		0·6		0·6		0·9
7	,, Oct. 1934		0·4		0·6		0·6		1·0
8	B & B, May, 1932		0·5		0·6		0·6		1·0
9	,, Jan. 1933		0·6		0·7		0·7		0·9
10	,, April, 1934		0·6		0·6		0·7		1·0
11	D & O, March, 1932		0·5		0·6		0·8		1·0
12	,, natural		0·5		0·6		0·8		1·0
13	,, Prismentha		0·4		0·5		0·8		0·8
14	American, Dec. 1932		1·6		1·6		1·6		1·4†
15	,, Aug. 1933		0·4		0·5		0·6		1·0
16	,, July, 1934		0·6		0·7		0·8		1·1
17	Mohawk, natural		0·6		0·7		0·9		1·2
18	,, rectified		0·6		0·7		0·9		1·2
19	"B," Oregon		0·4		0·5		0·5		0·5*
20	,, Michigan		0·5		0·7		0·8		0·9*
21	"C," natural		0·5		0·7		0·8		1·1
22	,, Wayne County		0·6		0·8		1·0		1·3
23	"D,"		0·4		0·4		0·8		0·8
24	Seattle, No. 1		0·6		0·8		0·9		1·2
25	,, No. 2		0·6		0·7		0·9		1·1

† From later results believed to be adulterated. * Authentic.

From the above results the observed red value after a 10-minute contact of oil and reagent seemed to show a remarkable constancy with American oils.

A fairly constant red value was also shown by samples of Italian and French oils, but within a different narrow range (Table II).

TABLE II

EUROPEAN OILS

				10-minute red value
26	Supplier	B	Italian	0·3*
27	,,	E	Italo-Mitcham	0·3
28	,,	F	,,	0·1
29	,,	G	,,	0·1
30	,,	F	Franco-Mitcham	0·1

* Authentic.

English oils gave somewhat more variable figures (Table III).

TABLE III

ENGLISH OILS*

					10-minute red value
31	Supplier	B	Lincs.		0·8*
32	,,	,,	Mitcham		1·2*
33	,,	H	Long Melford		0·5*
33*a*	,,	A	Cambridge,	1928	0·6
33*b*	,,	,,	,,	1929	0·7
33*c*	,,	,,	,,	1930	0·7
33*d*	,,	,,	,,	1931	0·4
33*e*	,,	,,	,,	1932	0·4
33*f*	,,	,,	,,	1932	0·5†
33*g*	,,	,,	,,	1933	0·4
33*h*	,,	,,	,,	1934	0·4

* All authentic specimens.

† Same crop as 33*e*, but adventitious weeds allowed to grow unchecked and harvested and distilled with the peppermint.

Even these results, however, were very low compared with those of Japanese oils. Table IV shows the values obtained with various oils, reputed to be Japanese, mostly bought in the open market, as there was no reason to suppose them not to be genuine. These gave much higher, but less constant, red values than any other group.

TABLE IV

JAPANESE OILS

			10-minute red value
34	Supplier	E	7·4
35	,,	J	5·7
36	,,	K	4·7
37	,,	M	6·2
38	,,	N	4·5
39	,,	P	5·6
40	,,	Q	5·7
41	,,	R	5·4
42	,,	H	7·3

This variation in red values of the different Japanese oils was not sufficient to interfere considerably with the order of accuracy which could reasonably be expected when attempts were made to make the method roughly quantitative. Table V shows the results from some mixed oils of known composition.

TABLE V

AMERICAN AND JAPANESE OIL MIXTURES

	10-minute red values							
Japanese oil used:	No. 35	36	37	38	39	41	34	62
American + 10 per cent. Jap.	1·2	1·2	1·2	1·3	1·3			
,, +20 ,, ,,	1·5	1·5	1·7	1·8	1·8	1·8	1·6	1·5
,, +30 ,, ,,	2·1	1·8	2·1	2·4	2·4			
,, +40 ,, ,,	2·4	2·2	2·4	2·8	2·8			
,, +50 ,, ,,	2·7	2·5	2·8	3·2	3·2			

It will be seen that mixtures containing amounts of Japanese oil likely to be used for adulteration had red values of the same order for equal proportions of different oils. From these results a roughly quantitative application of the test was evolved, and, on the basis of the figures obtained above, the following comparative table (VI) was constructed.

TABLE VI

RANGE OF VALUES FOR QUANTITATIVE ESTIMATION OF MIXED OILS

	10-minute red values	
	American	French and Italian
Containing 10 per cent. Japanese	1·1–1·4	0·6–0·9
20 ,, ,,	1·4–1·8	0·9–1·3
30 ,, ,,	1·8–2·4	1·3–1·9
40 ,, ,,	2·4–2·8	1·9–2·3
50 ,, ,,	above 2·8	above 2·3

For English oils the figures may be taken as similar to those for American oils, with the caution that, in view of the wider range shown for the pure oils in Table III, too much stress must not be laid on any results which slightly exceed these limits.

In order to test the method, mixed oils of unknown proportions were examined, with very satisfactory results. These are shown in Table VII. Specimens (*d*) and (*e*) were mixtures of oils not previously examined.

TABLE VII

UNKNOWN MIXTURES

	Red value (10 minutes)	Japanese oil	
		Found Per Cent.	Present Per Cent.
American (*a*)	1·9	30	30
(*b*)	1·2	10	10
(*c*)	0·7	nil	nil
(*d*)	1·9	30	33
(*e*)	2·5	40	50
(*f*)	2·1	30	20
(*g*)	2·4	35	30
(*h*)	1·2	10	10
(*j*)	0·9	nil	nil
English (*k*)	1·9	20	20
French (*l*)	1·2	20	20
(*m*)	2·0	40	40

The test was then applied to oils obtained from various wholesale houses, with the interesting results shown in Table VIII.

TABLE VIII

	Reputed American			Red value (10 minutes)	Japanese oil Found Per Cent.
43	Supplier	E	Hotchkiss	0·6	—
44	,,	E	Redistilled	1·3	10
45	,,	F	Feb. 1932	0·6	—
46	,,	F	Jan. 1933	0·5	—
47	,,	F	June, 1934	1·8	25
48	,,	F	Redistilled	1·5	20
49	,,	L		0·5	—
50	,,	J	Wayne County	1·6	20
51	,,	J		1·7	20
52	,,	K	Hotchkiss	0·7	—
53	,,	K	Wayne County	1·9	30
54	,,	E	Redistilled, Nov. 1934	0·9	—
55	,,	S		0·7	—
56	,,	S	Oregon	1·6	20
57	,,	T		0·5	—
	Reputed English and French				
58	Supplier	E	English	0·8	—
59	,,	J	,,	1·0	—
60	,,	K	,,	1·3	—
61	,,	K	French	0·2	—

By comparison with the figures in Table VI, it would appear that seven of the fifteen samples of American oil examined were adulterated with from 10 to 30 per cent. of Japanese oil. This is not an unexpected result, as the extent of the sophistication is undoubtedly wide, although one is placed in a position of considerable difficulty in condemning such a large proportion of oils.

Rectification of Japanese oil lowered the red value, but not sufficiently to affect materially the value given in mixtures.

TABLE IX

RECTIFIED JAPANESE OILS

				Red value (10 minutes)
62	Supplier	E	Rectified	4·9
63	,,	R	Double rectified	3·0
64	,,	H	Rectified	5·7

Oil 62 was used to adulterate American (*b*), English (*k*) and French (*m*) oils shown in Table VII.

The furfuraldehyde was found in the lower-boiling fractions, and elimination of these by fractionation produced oils with smaller red values. Hence, if these oils were used, quantitative results would indicate a rather smaller degree of adulteration than would actually be the case; thus any inaccuracy would be in favour of the supplier. Although experiments on a small scale in the laboratory gave an oil of low furfuraldehyde content when the first 5 per cent. of the steam distillate was rejected, this result was not supported by fractionations of 10 gallons of oil. Highly rectified oils, bought from a wholesaler, had low red values. The results are tabulated in Table X.

TABLE X

FRACTIONATED JAPANESE OILS

		Red value (10 minutes)
(1)	Original Japanese oil	4·0
(2)	Five per cent. distilled from (1)	6·2
(3)	Residue distilled	0·6
(4)	Five per cent. distilled from (3)	1·2
(5)	Residue from (4) distilled	0·2
(6)	"L," 10-gallon batch, 5 per cent. rejected ..	3·8
(7)	"L," rejected 5 per cent. from (6)	6·1
(8)	"D," Japanese oil, light fraction 10 per cent. ..	8·0
(9)	"D," ,, ,, middle ,, 80 ,, ..	3·2
(10)	"D," ,, ,, heavy ,, 10 ,, ..	2·6
(11)	Supplier H, rectified soluble Japanese oil ..	0·8
(12)	,, H, terpeneless ,, ,, ..	0·9

Distillation of Japanese oil over 5 per cent. potassium hydroxide solution also yielded oils with very low red values, but no trouble is anticipated with these oils, as they lost their aroma and developed an odour of terpenes, which was not concealed when mixed with American oil; the specific gravity of the oil was also lowered, sometimes appreciably; *e.g.* in No. 41 the sp.gr. fell from 0·8971 to 0·8926 after distillation over potash. Analysts may still rely on odour, taste and the usual chemical constants for the presence of these oils.

There appears to have been no previous reference made in the literature to the presence of furfuraldehyde in peppermint oil, although it has been recorded as being present in clove, cinnamon bark, bois de rose and a few others. It was at first thought that the crude methods of distillation employed in Japan and China might possibly account for the origin of the relatively large amounts of furfuraldehyde found in Japanese oil. Other oils, however, generally said to be prepared by primitive methods of distillation, gave a positive reaction in only a few cases when the test for furfuraldehyde was applied, and some oils known to be prepared by modern processes gave strong reactions. Hence it would seem probable that the furfuraldehyde is a natural constituent, and this view appears to be supported by the fact that furane derivatives and other compounds containing oxygen ring systems (*e.g.* carlina oxide, elsholtzione and cineole) occur in essential oils.

As a matter of interest, some 60 different oils were subjected to the aniline acetate test described above, with encouraging results. The extension of the test to detect some other adulterants is a possibility, especially for clove in pimento, and light camphor in rosemary oil. Further tests are being carried out, and it is hoped to make a subsequent communication on this point.

SUMMARY.—(i) Furfuraldehyde has been detected in peppermint oil, and the quantity present has been found to be variable with different types of oil, but approximately the same for all oils of the same type.

(ii) By use of this fact a tentative test has been devised to detect Japanese oil in genuine peppermint oils.

(iii) A roughly quantitative test has been developed.

(iv) The applicability of the reaction to the detection of specified adulterants in other essential oils is probable.

I wish to express my thanks to Messrs. Chivers & Sons, Ltd. (through Mr. T. Rendle), for most of the specimens of English oil, to Mr. E. J. Parry, Messrs. W. J. Bush & Co., and especially to Mr. C. T. Bennett, for many samples of genuine oils, and to Mr. C. J. Regan, for useful criticism.

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DISCUSSION

Mr. E. J. PARRY said that he had supplied Dr. Garratt with many peppermint oils of absolutely known composition, and he could say at once that the test definitely detected, reasonably quantitatively, mixtures which he, Mr. Parry, knew, and which Dr. Garratt did not. Numerous samples for which he, the speaker, had searched America, and which were, as definitely as man could say, perfectly pure peppermint oils, had passed this test satisfactorily. Of course, the trouble was that, although it was a step in the right direction, which might be useful experimentally, they were dealing here with a small quantity of impurity which could be eliminated directly some of those who were adulterating peppermint oils knew what they had to meet. He was afraid that as soon as Dr. Garratt's paper was published there would be a definite attempt to alter the fractionation of Japanese peppermint oils, in order to get rid of the small quantity of furfural. It would be quite easy to eliminate this fraction, and the reaction would then probably not be given. The positive reaction with American oil was so pronounced that one could not possibly discriminate between genuine American oil and one containing, say, 25 per cent. of Japanese oil, but if the reaction mixture were allowed to stand, the remaining colour was indicative of the percentage of the two oils used.

Mr. C. E. SAGE pointed out that even English peppermint oils which had not been redistilled contained some furfural. If further experience confirmed the results, the test would be a valuable addition to the few available tests for obtaining an indication of the presence of Japanese mint oil.

Mr. C. T. BENNETT, after congratulating Dr. Garratt upon his quantitative method of using the colour reaction, said that he had had the opportunity of applying the test to numerous oils, and had found that peppermint oils of authenticated origin gave either no reaction or, at most, very low figures. He agreed with Mr. Parry that it would not be difficult to remove the substance that gave the colour reaction. He hoped that the author would extend the test to other essential oils.

Mr. T. RENDLE thought that Dr. Garratt had helped forward the detection of adulteration of American peppermint oil. Unfortunately the sophistication of English oils was not unknown. He was, however, glad to notice from the figures given for English oil, that, with one exception, the furfural value was quite low. He thought that this one exception should be noted, as it would be disconcerting if a genuine oil of this character were condemned as containing Japanese oil because of its comparatively high furfural-content. Since it was difficult in growing peppermint for distillation to keep it free from adventitious weeds, it was interesting to notice from Dr. Garratt's results that when such weeds were distilled with peppermint, they were without influence on the furfural-content of the oil.

Dr. GARRATT, replying, said that the test was put forward only as a tentative one, and he did not suggest that it would end adulteration with Japanese oil. He was aware that it would be possible to circumvent the test, but in doing so manufacturers would have to take more trouble to adulterate their oils; it would cost more, and in any case the mint oil they produced would have a better flavour than the original Japanese oil. Much reliance was placed upon flavour, and to the expert the taste of Japanese oil was very poor. It was not probable that English oils would be adulterated with Japanese mint oil; it was more likely to occur with American oils. The presence of weeds in a crop might affect the oil, and chemical differences between oils grown in different localities might occur. An illustration of this was afforded by the fact that *M. arvensis* grown in Ceylon had an odour of spearmint.

The Determination of Copper in Foods with Special Reference to Milk

BY N. D. SYLVESTER, M.SC., A.I.C., AND L. H. LAMPITT, D.SC., F.I.C.

STATEMENTS regarding the effect of copper in stimulating the development of "tallowy" or "off" flavours in milk are numerous, and to a certain extent varied. Investigations of this problem demand a method capable of determining copper in small amounts, and also require a knowledge of the normal amount of copper in milk, with an idea of its possible range of variation.

This natural copper-content of milk has been a subject of considerable interest to chemists and to biochemists during recent years, and the methods of determination have been much investigated. The problem is complicated by the presence, in the ash, of considerable amounts of calcium and magnesium phosphates, and by the fact that the copper-content itself is very small.

The desirability of separating the copper from the rest of the inorganic constituents is admitted by most workers, and the methods previously employed may be summarised as follows:—

(i) Separation of copper as sulphide; (ii) separation by precipitation of calcium, etc., with ammonium hydroxide; (iii) electrolysis.

The first two, at least, of these processes have been criticised by various workers and stated to give unsatisfactory results, whilst, on the other hand, other workers have considered them to be reliable and satisfactory. There exists, therefore, an element of uncertainty as to the efficacy of the methods used and of the results obtained.

Recently, since the present work was commenced, a fourth method of separation has been used by Tompsett,[1] in which the copper is extracted with ether as the diethyldithiocarbamate compound from an ammoniacal solution of the milk ash, containing sufficient sodium citrate to prevent precipitation of phosphates. The possible interference by other metals was not apparently investigated.

The method which is to be described has been in use in the Lyons' laboratories for some time, and has been found to be accurate and sensitive. Briefly, it depends upon the quantitative extraction of copper from an acid solution by means of a chloroform solution of diphenylthiocarbazone—a procedure first recorded by Fischer and Leopoldi,[2] and used by them for the determination of copper in metals. After removal of the chloroform, the residue, which contains the whole of the copper, is digested with sulphuric and perchloric acids, and copper is determined colorimetrically by means of sodium diethyldithiocarbamate, a reagent first used by Delépine[3] and subsequently by Callan and Henderson.[4]

The method is simple in execution and avoids the laborious ammonium hydroxide separation, which is particularly troublesome in the case of milk powders. Equally it avoids the alternative hydrogen sulphide precipitation, which is certainly not accurate unless careful attention is given to a number of important factors.

The results which will be given in the present paper have been obtained entirely on milk, but the method is applicable to other foods and, in fact, has been so used.

DETAILS OF THE EXPERIMENTAL TECHNIQUE.—Ash the sample with a small amount of A.R. concentrated sulphuric acid in a silica dish at 500° to 550° C. in a muffle furnace. The dish should preferably be covered with a silica plate in order to prevent accidental contamination. (In the case of milk, 20 g. are evaporated to dryness in a silica dish after the addition of a few drops of $5N$ sulphuric acid, which curdles the sample and assists in the evaporation. The residue is then ashed with 2 ml. of A.R. concentrated sulphuric acid.) Dissolve the ash in 5 ml. of $6N$ hydrochloric acid and heat to boiling. Dilute with 10 ml. of water and heat to boiling, ensuring complete solution of the ash. After cooling, wash into a separating funnel with two lots of 10 ml. of water.* Add $5N$ ammonium hydroxide carefully until the solution is just neutralised and then add 1 ml. of $6N$ hydrochloric acid. Extract the copper from this solution by shaking vigorously with 3 lots of 5 ml. of diphenylthiocarbazone reagent or, when necessary, until the colour of the 5-ml. portion in use is not affected. (A reddish-purple colour appears in the chloroform layer when sufficient copper is present.) Wash the extracts with 10 ml. of water, using the same water for successive washings of the separate chloroform extracts.

Combine the extracts in a Pyrex boiling tube (about 8″ × 1″) and distil off the chloroform. Add 1 ml. of A.R. concentrated sulphuric acid and 3 or 4 drops of 60 per cent. A.R. perchloric acid. Boil until colourless. (The addition of a little more perchloric acid may be necessary when large amounts of diphenylthiocarbazone reagent have been used.) Dilute the residue with about 15 ml. of water.* Make the solution just alkaline with $5N$ ammonium hydroxide (about 7 ml.) and, after cooling, pour into a 100-ml. Nessler cylinder, rinsing the tube with water until the volume is about 50 ml. Prepare a blank solution in a second cylinder (which must match the first cylinder exactly) using 2·5 g. of A.R. ammonium sulphate and water up to 50 ml. Add 3 ml. of $5\,N$ ammonium hydroxide to each cylinder and 5 ml. of sodium diethyldithiocarbamate reagent. Add dilute standard copper solution from a micro-burette to the blank cylinder until the yellow colour is not quite matched. Adjust the liquid levels in the tubes so that they are identical, and add to each an amount of A.R. amyl alcohol depending on the amount of copper present. Ten ml. are sufficient for copper-contents up to 1·5 ml. of standard copper solution. Shake each cylinder vigorously, covering the top with the palm of the hand, and allow to settle. Observe the colour of the upper amyl alcohol layer by viewing horizontally and match exactly by the addition of further standard copper solution, shaking both cylinders after each addition. Correct for the copper-content of the reagents by making a control determination from the beginning to the end.

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* When the copper-content is known to be high an aliquot portion of the solution may be taken, containing preferably not more than 0·05 mg. of copper.

1·0 ml. of dilute standard copper solution ≡ 0·01 mg. Cu ≡ 1·0 part per million on a 10-g. sample.

Reagents	
1. Distilled water.	Distilled water must be free from copper.
2. $6\,N$ hydrochloric acid.	This reagent should be free from copper and it has been found convenient to use the constant boiling acid distilled from glass apparatus.
3. $5\,N$ ammonium hydroxide.	Dilute 0·880 ammonia with copper-free distilled water. It is convenient to have the strength fairly accurate.
4. Diphenylthiocarbazone reagent.	A 0·15 per cent. solution in chloroform is prepared without heating, and it is freed from copper by the following process. Place 100 ml. of chloroform solution and 100 ml. of water in a separating funnel. Add 5 ml. of 0·880 ammonia and shake vigorously. Discard the chloroform layer and wash the alkaline liquid with two lots of 5 ml. chloroform. Then add 200 ml. A.R. chloroform and hydrochloric acid until the aqueous layer after shaking is colourless. Run off the chloroform solution and store in a brown glass bottle.
5. Sodium diethyldithiocarbamate reagent.	Prepare a 0·1 per cent. solution in cold distilled water and filter into a brown glass bottle ready for use. The reagent should be freshly prepared after about 1 week.
6. Standard copper solution.	Prepare a solution containing 1·964 g. $CuSO_4.5H_2O$ and 2 or 3 drops of concentrated sulphuric acid per l. Dilute this solution 50 times to give a dilute standard copper solution of which 1·0 ml. ≡ 0·01 mg. of copper.

NOTES ON THE METHOD.—(i) *Precautions.*—In the case of determinations of very small amounts of copper, every possible precaution should be taken at all stages of the method to prevent accidental contamination. For example, dust from the atmosphere is particularly to be avoided, and dishes should therefore be covered with silica plates during ashing in the muffle furnace.

The copper-content of the blank determinations must obviously be reduced to a minimum either by selection of suitable copper-free reagents, or, where it is more convenient, by purification of available reagents.

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* When the copper-content is known to be high an aliquot part of the solution may be taken, containing preferably not more than 0·05 mg. of copper.

(ii) *The Method of Destruction.*—No work has been done by the present authors to determine the maximum permissible temperature for ashing. In view of the statements in the literature that copper is lost at high temperatures, it was thought desirable to ash at as low a temperature as is conveniently possible. Even so, the temperature used, namely, 500–550° C., is not so low as various authors have claimed to be desirable (*e.g.* McFarlane[5] 380–400° C. and Ansbacher *et al*[6] 400° C.).

As a check on the results obtained by the silica dish method of ashing, determinations were made on the residue from sulphuric acid digestion, with the following typical results:—

		Ashing in silica dishes at 500°–550° C. p.p.m.	Sulphuric acid digestion p.p.m.
Copper-content determined on 20 g. of pure milk.	1.	0·10	0·02
	2.	0·14	0·08
	3.	0·13	0·10

In spite of every precaution which could be taken to prevent possible contamination, the results obtained by ashing in silica dishes were consistently higher than those obtained after the sulphuric acid digestion. It was concluded that small amounts of calcium sulphate, which remained insoluble during the extraction of the copper by means of the carbazone reagent, adsorbed and prevented the extraction of a small and variable amount of copper.

This supposition was proved to be correct by the application of a method devised by Dyer and recently published by Lynch *et al*[7] for the quantitative separation of lead from calcium phosphate, preparatory to the determination of lead in bone. The method is equally applicable to the determination of copper, and their instructions were followed without modification, except as regards amounts of reagents. The determinations were made on 20 g. of homogenised milk, and copper was determined on the final solutions by the method already described. The results agree perfectly with those obtained by ashing in silica dishes.

Ashing in silica dishes at 500°–550° C. p.p.m.	Sulphuric acid digestion	
	Normal method p.p.m.	Dyer's method p.p.m.
0·16	0·09	0·15
0·21	0·17	0·22
0·18	0·13	0·17

It should be borne in mind that a sulphuric acid digestion will not introduce any serious error when the copper-content is high, or when calcium is not present in sufficient amount to form a precipitate of calcium sulphate in the solution to be extracted.

(iii) *The Possibility of Interference by Other Metals.*—The possibility of interference by the rarer elements has not been examined, but none of the ordinary metals considered in the usual group analysis interferes. Mercury is extracted by the carbazone reagent, but does not affect the colorimetric determination with sodium diethyldithiocarbamate.

The following table shows the recovery of added copper from milk in the presence of metals which are liable to be present in food:

Added copper p.p.m.	Other added metals p.p.m.		Copper found p.p.m.
0·52	Nil		0·53
*1·00	,,		1·05
1·51	,,		1·51
*2·00	,,		1·85
*3·00	,,		2·95
*1·60	Iron	50	1·55
*2·80	,,	,,	2·80
0·31	Aluminium	50	0·26
1·10	,,	,,	1·07
*3·20	,,	,,	3·30
0·38	Tin	50	0·37
1·04	,,	,,	0·98
*2·20	,,	,,	2·10
0·27	Lead	50	0·30
1·27	,,	,,	1·19
0·17	Zinc	60	0·20
*0·70	,,	,,	0·80
0·95	,,	,,	0·95
*0·70	Nickel	50	0·65
*2·70	,,	,,	2·65
0·22	Manganese	50	0·25
1·38	,,	,,	1·34

* These determinations were made on 10 g. of milk; the others were made on 20 g.

(iv) *The Colorimetric Determination.*—The final method of determination was chosen after considerable experience with other methods. The ferrocyanide method,[8] which is quite satisfactory for larger amounts, is not suitable for the determination of the small amounts of copper normally found in milk. The delicate pink colour which is obtained is developed slowly, and matching becomes very difficult.

The yellow colour obtained with copper in ammoniacal solution on the addition of sodium diethyldithiocarbamate can, of course, be matched directly. The method is, however, not as accurate as the one which has been adopted. In aqueous solutions the yellow colour is due to a colloidal precipitate, and such colorations are not eminently suitable for accurate matching. The colour shade is usually different in the blank from that which is obtained in the determination, and no appreciable improvement is effected by resorting to the practice of adding a stabiliser, such as gum arabic. The solution of the copper compound in an organic solvent overcomes this difficulty, and accurate results can be obtained in this way if the solution is shaken with amyl alcohol in the Nessler cylinder, the colour of the upper layer being viewed transversely. The necessity for using identical cylinders is of course obvious. The volume of amyl alcohol used can be varied according to the amount of copper present so that the colour of the layer is adjusted to a suitable intensity for matching. When 10 ml. of amyl alcohol are used, the addition of 0·02 ml. standard copper solution (*i.e.* 0·0002 mg. Cu) is readily detected when the amount of copper already present is not more than about 0·015 mg.

The colour of the upper layer could, of course, be measured in a suitable colorimeter, or in the Lovibond tintometer as suggested by Haddock and Evers,[9] and such a procedure might be preferable for larger amounts of copper.

(v) *The Standard Copper Solution.*—In the preparation of a standard copper solution, a few drops of sulphuric acid are added, in order to prevent deterioration of the solution. When the acid was omitted, the strength of the dilute standard copper solution, containing 0·01 mg. of copper per ml., was observed to fall considerably, owing to deposition of copper salts on the walls of the container.

THE NATURAL COPPER-CONTENT OF MILK.—In view of the widely different statements in the literature, it is of interest to record the natural copper-content of milk. The most recent determinations, namely, those of Conn *et al.*[10] and Tompsett[1] give values of 0·051 to 0·132 p.p.m., and 0·10 to 0·16 p.p.m., respectively. McFarlane[4] gives the copper-content of pure milk as 0·07 to 0·10 p.p.m. Tompsett, as already stated, extracted the copper direct from a solution of the milk-ash, using carbamate and ether, whereas a preliminary sulphide separation was used by the other workers mentioned.

Results obtained by the present method, using 20 g. of milk, are given below, together with details of the origin of the samples.* The cows were milked directly into glass bottles, and 0·15 ml. of formalin (previously tested for copper) was added to 50 ml. of milk as a preservative. Arrangements for taking the samples were made by Mr. E. B. Anderson, Chief Chemist to the United Dairies, Ltd., to whom our thanks are due for the interest which he has shown in the matter.

The figures given are the mean of duplicate determinations, none of which differed by more than 0·04 p.p.m.

	Name	Breed	Time	Quarters	Copper-content p.p.m.
1.	Blue cow	Blue Albion	a.m.	All	0·14
2.	—	Irish Shorthorn	,,	,,	0·17
3.	Lincoln	Devon Cross		Hind	0·10
4.	Blossom	Devon		Left fore	0·13
5.	Blue cow	Blue Albion		—	0·11
6.	Countess	Devon		All	0·13
7.	Darkie	Shorthorn		—	0·11
8.	Duchess	Devon		Hind	0·13
9.	—	Friesian		All	0·09
10.	Handsome	Shorthorn		All	0·11
11.	Mackham	Devon		Right hind	0·12
12.	Roan	Shorthorn cross with Devon		—	0·10
13.	Starface	Devon cross with Ayrshire		—	0·16
14.	Strawberry	Shorthorn		—	0·10
15.	Titch	—		Right hind	0·12
16.	Whiteface	Devon Cross		—	0·11

These results show the copper-content of pure milk to vary, in the case of the 16 samples here recorded, from about 0·09 p.p.m. to about 0·17 p.p.m., with a mean value of 0·12 p.p.m. The figures are in substantial agreement with those of Tompsett.

CONCLUSION AND SUMMARY.—1. A technique has been described, using diphenylthiocarbazone in chloroform as an extraction reagent, which enables the copper-content of food to be determined with accuracy.

2. In the case of milk, containing about 0·12 p.p.m., reliable duplicates can be obtained on a relatively small amount, such as 20 g., and the copper-content can be determined with an error of ± 0·02 p.p.m.

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* Taken in November, 1934.

3. The method has been proved to be applicable to food in general and its accuracy to be unaffected by the presence of the common metals, iron, tin, aluminium, lead, zinc, nickel and manganese.

4. The copper-content of sixteen samples of milk, drawn from the cows with precautions against copper-contamination, was found to range from 0·09 to 0·17 p.p.m., with a mean of 0·12 p.p.m. The cows were of different breeds and were situated in different parts of the country.

Our thanks are due to Mr. A. N. Ainsworth, B.Sc., A.I.C., for assistance in the practical work, and to Messrs. J. Lyons & Co., Ltd., in whose laboratories the work was conducted, for permission to publish.

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Selective Adsorption in the Examination of the Unsaponifiable Matter of Marine Oils

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THE ingenious method devised nearly thirty years ago by Tswett[1] for the separation by selective adsorption of the pigments of the chloroplast had been singularly little used for other purposes until Karrer, Winterstein and an associated group of investigators recently demonstrated that, with minor modifications, the method could be of great value in effecting the separation and concentration of various substances.

We have recently had occasion to study the unsaponifiable matter from a variety of oils and fats in connection with investigations on vitamins *A* and *E* which are in progress in this laboratory. In this work selective adsorption on aluminium oxide has proved of such great value that it is thought worth while recording a few of the results. We have already described how this method recently enabled us readily to separate and identify squalene as the constituent of the unsaponifiable fraction of olive oil which is responsible for the characteristic high iodine value.[2]

We owe it largely to the pioneer work of Tsujimoto, Toyama and their colleagues that the nature of the substances present in the unsaponifiable fraction of many interesting marine oils has been so satisfactorily elucidated.* By employing ordinary methods of chemical fractionation it is not always a simple matter satisfactorily to separate the individual substances which may be found together in such fractions. It was hoped that adsorption methods might prove more convenient. In the course of our studies three fish-liver oils and one fish oil were investigated.

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* This work is summarised in a paper by M. Tsujimoto (*J. Soc. Chem. Ind.*, 1932, **51**, 317.

Of all adsorbing materials we have tried, the special preparation of aluminium oxide made by Merck has given the most satisfactory results. Poured into a long glass tube in the form of a thick suspension in light petrol (b.p. 40–60° C.) it sediments to form an evenly packed column showing uniform drainage. It is most important to obtain even packing of the oxide and to ensure the absence of air bubbles from the column. A thin wad of cotton wool placed on top of the column of earth will prevent disturbance of the superficial layers when fluid is poured on. If this occurs, the boundaries between the zones will tend to be irregular. The column of oxide must never be allowed to drain dry, and it is advisable to keep it actually covered with a shallow layer of petrol until the actual adsorption is begun. For the solution of most unsaponifiable fractions light petrol is the best solvent. If the material is not readily soluble in this, a small amount of benzene may be added, but this tends to lessen adsorption generally and to permit the passage of substances which otherwise would be held by the earth. The solution of the material to be investigated is poured on to the top of the column and allowed to percolate slowly through the oxide, solvent being added as the level falls.

Usually the passage of the solution through the column results in the formation of clearly marked zones indicated by coloration of the oxide. As washing with the solvent progresses the position of these coloured zones may change, some tending to descend the column slowly and in due course to pass out into the filtrate. Washing is normally continued until no further change in the position of the zones appears to be taking place. Considerable quantities of solvent are usually required for washing. Adequate washing is essential in order to obtain good separations. The filtrate, or filtrates if, as is often the case, there have been reasons for separating the washings into more than one fraction, are evaporated down *in vacuo*. The column of oxide is divided—usually, it must be admitted, on a visual basis which may possibly at times be misleading—and the separate batches of oxide are eluted before the adherent light petrol has evaporated. It must be remembered that many of the constituents of the unsaponifiable fraction of oils are readily oxidised by exposure to air (*e.g.* lipochrome pigments) and that such oxidation will occur very rapidly if the finely divided oxide becomes dry. In our experience the best eluting fluid is a mixture of 50/50 or 75/25 methyl alcohol and ether. Methyl alcohol and benzene mixtures are also good.

The solutions of eluted material are evaporated down with precautions against oxidation. If the adsorbent oxide retains colour after treatment with the eluting fluid, the presence of acidic pigments of the astacene type is indicated. In such cases a second elution with methyl alcohol acidified with hydrochloric acid or with slightly acidified chloroform will usually remove the residual adsorbed material.

The separation of the column calls for a certain amount of judgment based on experience. Usually one is tempted to base it on a division between the various coloured zones which most columns show. In many cases this is satisfactory; a good example is the separation of the constituents of the unsaponifiable fraction of wheat-germ oil which has recently been described (Drummond, Singer and Macwalter[3]). In others it may be misleading, in that the various zones do not show sharp differentiation with regard to the type of substances adsorbed. When the material being submitted to the process is very slightly coloured or actually colourless, it may be difficult to decide at which points to divide the column, as it will in all probability show no clearly defined zones. Professor C. K. Ingold suggested to us that in such cases it might be possible to observe differentiation by conducting the adsorption in a silica tube and subsequently examining for fluorescence in ultra-violet light. We did not have occasion to try this interesting suggestion, but that the method is actually a practical one is shown by its having been independently employed successfully by Winterstein and his colleagues in the separation of polycyclic hydrocarbons.[4]

When aluminium oxide is employed as the adsorbent and light petrol as the solvent it will be found, generally speaking, that saturated hydrocarbons pass most readily through the column. Almost as easily, unsaturated hydrocarbons, at any rate those of the squalene type, pass into the filtrate. In this fraction β-carotene will appear. Unsaturated alcohols tend to be washed down into the lower layers of the columns, but their distribution is, to some extent, determined by the nature of the other substances present. A relatively large proportion of highly unsaturated hydrocarbon (squalene) will, so far as our experience shows, tend to bring the unsaturated alcohols lower down the column, and may cause some leakage through to the filtrate. Sterols tend to be adsorbed in a relatively well-defined belt situated in most cases about one-third of the distance from the top of the column. With the sterol certain lipochromes of the xanthophyll type may often be associated or, if not, will usually be found concentrated in neighbouring zones. Saturated alcohols are usually held at the top of the column.

EXPERIMENTAL.—The liver oils examined were (A) "Greenland" shark-liver oil, (B) "Japanese" shark liver oil and (C) rat-fish liver oil. (A) and (B) were commercial products, stated to be genuine unadulterated specimens. The sample of rat-fish liver oil was prepared in a laboratory by direct steam-extraction of a batch of livers from *Chimaera monstrosa.** The fourth oil examined was an authentic sample of Icelandic herring oil. The characteristics of the oils are shown in Table I.

(A) UNSAPONIFIABLE MATTER FROM "GREENLAND" SHARK-LIVER OIL.—Prepared in the usual manner, this was a viscous yellow fluid containing about a quarter of its weight in the form of material precipitated by digitonin (sterol). The greater part of this was removed by crystallisation from methyl alcohol at 0° C., the mother liquors being subsequently concentrated down to approximately half the original volume and again cooled to 0° C. The first group of crystals consisted almost entirely of cholesterol, but that obtained from the subsequent crystallisation was clearly different in character. After only one recrystallisation from methyl alcohol the m.p. was 64–66° C. Two re-crystallisations from ether raised the m.p. to 68·5° C., which suggested the identity of the substance with batyl alcohol—an impression which was fully confirmed by further examination.

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* We are indebted to Mr. F. Lawson of the British Cod Liver Oil Producers, Hull, for kindly preparing and supplying the sample of rat-fish liver oil. Samples (A) and (B) were supplied by the courtesy of Messrs. Boehms, Ltd. The sample of herring oil was obtained from H./F. Kveldislfur, Reykjavik, Iceland.

TABLE I

	Shark-liver oil		Rat-fish liver oil		Iceland Herring oil
Oil	(A) "Greenland"	(B) "Japanese	Sample I	Sample II	
Saponification value	143·1	171·7	152	157	188
Iodine value	110	106	96	99	130
Refractive index, n_D^{40}	1·467	1·470	1·461	1·462	1·472
Unsaponifiable matter, per cent.	22·7	12·25	29·0	28·0	6·66
Antimony trichloride test (B.P. method)	72	75	0	0	Very slight blue colour
Specific gravity	0·9075	0·915	0·8896	0·8942	0·9174
Unsaponifiable matter					
Iodine value	80·8	70	71	—	75
Antimony trichloride test (B.P. method)	700	785	—	—	8·4
Vitamin *A* (by spectroscope), per cent.	0·95	1·17	—	—	—
Cholesterol, per cent.	25·7	1·43	4·9	—	45·4

After removal of the crystals of sterol and of batyl alcohol there remained a semi-soluble material corresponding to approximately 6 per cent. of the original oil. This material was dissolved in a small quantity of light petrol, and the solution was slowly drawn through a column of adsorbent aluminium oxide (Merck). A certain amount of "zoning" was observed, and washing with light petrol was continued until no further change occurred in the distribution of the visible zones. The material which passed through the column without adsorption was collected separately and the solvent removed. The column of oxide was divided to correspond with the four zones of adsorption, each of which was separately treated with methyl alcohol containing a small proportion of ether, in order to elute the adsorbed material. The fatty materials were subsequently recovered from the solvents. In Table II are set out the results of an experiment in which material was treated in a column of aluminium oxide approximately 10 in. in height and 0·75 in. in diameter.

TABLE II

Fraction	Weight g.	Iodine value	Appearance
Material from filtrate (not adsorbed) (Fr. 1)	1·74	152·5	Mobile, lightly coloured
Bottom zone of the column (least adsorbed) (Fr. 2)	2·18	82·5	Yellowish heavy liquid
2nd zone from bottom (Fr. 3)	2·95	75·9	Semi-solid, dark brown
3rd zone from bottom (Fr. 4)	2·05	72·3	Heavy yellow liquid
Top zone (Fr. 5) (most adsorbed)	1·79	77·0	Pale, heavy liquid

When adsorbing from light petrol solution, any hydrocarbons in the unsaponifiable matter will tend to pass through the column and appear in the filtrate. The rather high iodine value of Fr. 1 suggested the presence of squalene, and treatment with hydrochloric acid in dry acetone soon confirmed this suspicion. Characteristic crystals of the hydrochloride (m.p. 112–114° C.) were obtained. Accompanying the squalene was an unsaturated alcohol, almost certainly selachyl alcohol. The examination of the adsorbed fractions showed that in all cases they consisted almost entirely of an unsaturated alcohol. Small amounts of batyl alcohol were isolated from the top zone of the column (Fr. 5) and of sterol from Fr. 4, but it was clear that most of the adsorbed material consisted of an unsaturated alcohol. This was easily proved to be selachyl alcohol by hydrogenation. The fractions, after removal of any solid material (batyl alcohol or cholesterol) by crystallisation from methyl alcohol, were reduced with hydrogen and palladium in alcohol solution at room temperature. The reductions proceeded smoothly and yielded almost quantitative yields of batyl alcohol.

(B). UNSAPONIFIABLE MATTER FROM "JAPANESE" SHARK-LIVER OIL.—Fifteen g. of this material were dissolved in about 50 ml. of light petrol and passed through a column of Merck's aluminium oxide about 10 in. in height and 0·75 in. in diameter. Four distinct zones appeared, all tending to move slowly down as washing with the solvent progressed. About 2 l. of petrol were used for washing. The column of oxide was divided into the four zones, and the adsorbed material was eluted with methyl alcohol containing a small amount of ether. The character of the fractions obtained is set out in Table III.

TABLE III

Fraction	Weight g.	Iodine value	Appearance
1. Material from filtrate (not adsorbed) ..	7·03	106·0	Mobile, yellow liquid
2. Bottom zone of column (least adsorbed)	0·086	105·0	Mobile, yellow liquid
3. 2nd zone from bottom	1·01	84·3	Orange-yellow liquid
4. 3rd zone from bottom	2·93	81·6	Orange-yellow liquid
5. Top zone of column (most adsorbed) ..	3·67	39·0	Yellow liquid with crystals

It will be observed that nearly half the original material passed through the oxide. This fraction was a mobile, yellow oil which, on superficial examination, appeared to consist of an unsaturated alcohol and squalene. Fractional distillation at 0·4 mm. effected a separation of the former and further concentration of the hydrocarbon.

TABLE IV

	Temperature ° C.	Weight g.	n_D^{40}	Iodine value
Fraction 1*a* ..	180–190	1·27	1·4450	71
Fraction 1*b* ..	190–200	1·71	1·4470	85
Fraction 1*c* ..	200–210	0·94	1·4500	136
Fraction 1*d* ..	210–220	0·84	1·4570	144
Fraction 1*e* (Residue)		0·82	1·4730	143

Fractions 1*a* and 1*b* appeared to consist mainly of one substance, an unsaturated alcohol; accordingly, they were combined and subjected to reduction by hydrogen and palladium. A good yield of octadecyl alcohol was obtained, which indicated that the original substance was oleyl alcohol. The fractions of higher b.p. (1*c* and 1*d*) gave yields of squalene hydrochloride on treatment with hydrochloric gas in dry acetone. From this it appears that the material which passed through the adsorbing column consisted of a mixture of oleyl alcohol and squalene.

The material eluted from the lowest zone (Fr. 2) of the column was found to be almost identical in character. The two zones above this (Fr. 3 and 4) yielded an orange-yellow liquid, from which a small amount of crystalline material separated on standing. It was separated satisfactorily by crystallisation from methyl alcohol and readily identified as cholesterol.

After removal of the sterol at −14° C. the solvent was evaporated. The residue was a yellow oil behaving like an unsaturated alcohol, probably selachyl. On reduction with hydrogen on palladium a white crystalline product separated out in the reaction vessel. It was fully identified as batyl alcohol; the conclusion is justified, therefore, that its unsaturated precursor was selachyl alcohol.

The topmost zone (Fr. 5) was a viscous, almost colourless fluid, from which crystals separated on standing. These were more satisfactorily obtained by crystallisation from methyl alcohol. Their identity as batyl alcohol was readily established. The small portion soluble in methyl alcohol proved to be selachyl alcohol, as it yielded batyl alcohol on hydrogenation.

(C). UNSAPONIFIABLE MATTER FROM LIVER OIL OF RAT-FISH.—The unsaponifiable matter was a viscous, pale yellow oil, from which, on standing, a white crystalline material separated. By treatment with methyl alcohol at 0° C. the separation of this compound was facilitated. It proved to be chimyl alcohol, m.p. 61–61·5°. The material soluble in methyl alcohol was a viscous, yellow oil. Fifteen g. were dissolved in 50 ml. of light petrol and run through a 10-in. column of aluminium oxide, the oxide being afterwards washed through with about 2 l. of petroleum spirit. The fractions obtained are given in Table V.

TABLE V

	Weight g.	n_D^{40}	Iodine value	Appearance
1. Filtrate (not adsorbed)	6·97	1·4605	124	Mobile, slightly yellow
2. Bottom zone (least adsorbed) ..	1·21	1·4630	76	,,
3. 2nd zone from bottom	2·66	—	76	Yellow, semi-solid wax
4. Top zone (most adsorbed) ..	3·90	—	—	,,

The material from the filtrate was a mobile, slightly yellowish liquid which, on treatment with hydrochloric acid gas in dry acetone solution, showed the presence of squalene. The yield of squalene hydrochloride, m.p. 112–116°, was such as to indicate that the remainder of the fraction was composed of a substance with an iodine value about 70. As the general behaviour of this fraction indicated the presence of selachyl alcohol, some of it was hydrogenated with palladium catalyst at room temperature. A satisfactory yield of a white crystalline product was obtained, the identity of which as batyl alcohol was readily established.

Fraction 2 proved to be an almost pure selachyl alcohol by similar reduction to batyl alcohol. The greater part of Fr. 3 proved to be cholesterol, the small amount of residual oily material being in all probability selachyl alcohol. The top zone, Fr. 4, yielded on recrystallisation from methyl alcohol, a small amount of pure batyl alcohol, the mother liquors yielding an oil, with an iodine value of 70, which appeared to be selachyl alcohol. On hydrogenation it gave the expected yield of crystalline batyl alcohol.

(D). UNSAPONIFIABLE MATTER FROM HERRING OIL.—After removal of most of the sterol (cholesterol) by recrystallisation from methyl alcohol at 0° C. the residual fraction (2·5 g.), which was a yellow oil, was dissolved in about 50 ml. of light petrol and passed through a column of aluminium oxide; washing with this solvent was maintained until about 1 l. had passed through the column. The fractions obtained are set out in Table VI.

TABLE VI

	Weight g.	Iodine value	Appearance
1. Filtrate, material unadsorbed ..	1·2484	80	Yellow liquid
2. Bottom band in column (least adsorbed)	0·5182	78	Pale, yellow solid
3. Middle band in column	0·2992	67	Soft, crystalline wax
4. Top band in column (most adsorbed)	0·1282	65	

Fraction 1 was a yellow liquid (iodine value 80). On crystallisation from methyl alcohol a small quantity of cholesterol separated. The methyl alcohol was removed, and the residue of yellowish liquid was freed from sterol by precipitation with digitonin. The iodine value was now 92. As this oily liquid behaved like an unsaturated alcohol, it was subjected to hydrogenation. It gave a good yield of a crystalline, white solid which, after purification, was fully identified as octadecyl alcohol.

Fraction 2 was a pale yellow solid (iodine value 78). It consisted mainly of cholesterol. The residue, a yellowish liquid (iodine value 92), was too small in amount to permit of further examination.

Fraction 3 was distinctly crystalline, and was also found to consist almost entirely of cholesterol.

The aluminium oxide of the top zone (Fr. 4) was deep red-violet in colour. The usual attempt to elute with methyl alcohol and a trace of ether failed to remove all the adsorbed material. It removed a certain amount of sterol, but the red pigment remained held fast. This behaviour recalled that of the acidic lipochrome pigment of the astacene type, and accordingly elution with chloroform after acidification with hydrochloric acid was tried. This readily removed the pigment, solutions of which showed two broad absorption bands with maxima at 412 and 500$m\mu$. The latter is almost certainly attributable to astacene, but the substance responsible for the other band has not been detected.

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A Moving Mercury Cathode Apparatus*

By B. S. EVANS, M.C., D.Sc., F.I.C.

The ordinary form of mercury cathode apparatus consists of a beaker containing a pool of mercury on the bottom; the current is led in through a platinum wire sealed into a glass tube, through the end of which it just projects, this projecting end being totally immersed in the mercury, so that the platinum does not come in contact with the electrolyte. The electrolyte is contained in the beaker and floats on the surface of the mercury; the anode consists of the platinum apparatus normally used as a rotating cathode, which is made to revolve in the electrolyte to provide the necessary agitation. This apparatus is used solely to remove undesired metals from solution, the ultimate determination being carried out on the metal or metals remaining in the electrolyte (*e.g.* aluminium in aluminium brass or vanadium in vanadium steel). When the electrolysis is completed the electrolyte is recovered by syphoning it off and repeatedly washing the mercury by pouring in hot ammonium sulphate solution and again syphoning; a possibly preferable form of apparatus allows of the removal of the mercury through a tap in the bottom of the vessel; this, however, is possible only where the mercury has not become too viscous owing to the metals dissolved in it as a result of the electrolysis.

This apparatus is open to several criticisms:

(*a*) The greater number, if not the whole, of the amalgams ordinarily dealt with are lighter than mercury, and therefore tend to float on the surface of the cathode; hence the cathode operates under the least economical conditions possible, *i.e.* the surface of deposition is fully saturated with the metal depositing, and transference of the latter to the bulk of the mercury can take place only by diffusion, whilst any re-solution of the metal is favoured.

(*b*) The platinum electrode used as anode has to be fairly massive (and therefore expensive) to stand the stresses set up by the rather rapid rotation which is essential. True, the agitation may be provided by a glass stirrer separate from the anode, but this introduces unnecessary complication into the apparatus.

(*c*) To provide efficient stirring the anode must be fairly well immersed in the electrolyte (again the use of a glass stirrer evades this point); hence it is impossible to apply a very high anode current density. As the anode oxidising effect tends to rise when the current density falls, this may be a point of vital importance (*e.g.* in presence of manganese there is continuous production of permanganate or manganese dioxide which has to be dispelled with a reducing agent; also, an equilibrium seems to be set up below which it is impossible to remove further manganese).

(*d*) A mechanical stirring appliance is necessary.

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* Communication from the Research Department, Woolwich.

(*e*) Where an ordinary beaker is used to contain the electrolyte, the latter has to be syphoned off with the current running; this in itself is a somewhat clumsy device and, in view of the washing with ammonium sulphate solution, the resulting liquid is large in volume and contains a considerable amount of ammonium salts.

(*f*) Even if required, a porous diaphragm cannot be used to surround the anode if the latter is stirring the liquid [see (*b*)].

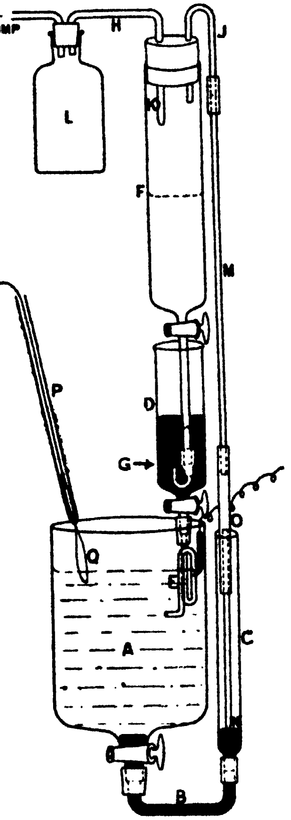
(*g*) The current passed is rather large.

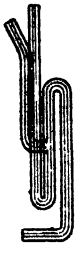
The apparatus about to be described is based on what I believe to be an entirely new principle. The cathode consists of a thin thread of mercury projected across the electrolyte; this mercury falls to the bottom of the vessel containing the electrolyte, passes through a tap, round a U-shaped tube, and is then carried up in an air-lift; it then passes into a separating funnel containing a solution designed to remove (at any rate partially) the metal dissolved in the mercury, and from there flows into the reservoir supplying the cathode jet. Hence the mercury is in continuous circulation, and the cathode always in movement and always supplied with relatively clean mercury; in addition to the fact of the cathode moving through the electrolyte, as the stream is directed somewhat to one side of the electrolyte vessel, the electrolyte itself is set in motion and an efficient stirring is maintained. The jet of mercury being very thin and not very long (say 30 mm. × 0·5 mm.), the cathode current density is naturally very high with the current used (0·5 to 0·8 amp.); this appears to be an advantage. In order to keep the anode current density high, for reasons stated above, the anode is formed of a loop of thin platinum wire dipping a little below the surface of the electrolyte; with a 20-volt circuit no rheostat is required, the supply of current being regulated by raising or lowering the anode wire, thus keeping the anode current density at a maximum. The total amount of platinum required for the anode and for the cathode lead-in is about 8 inches of thin wire; the amount of mercury necessary is about 50 ml. The electrolyte is easily removed from the apparatus at the end of the electrolysis by running the mercury in the bottom of the vessel just below the tap, and pouring the aqueous liquid into a beaker. As the anode is stationary and very small, and only dips a little way into the electrolyte, it might readily, if required, be surrounded with a minute porous diaphragm too small to introduce appreciable error into analytical operations subsequently carried out on the electrolyte; this might conceivably be a great advantage.

Details of the construction of the apparatus are as follows:

The electrolysis vessel, A, can be easily made by cutting down a large separating funnel to convenient dimensions; it is essentially a beaker with a tap at the bottom; the stem of the funnel is also cut down to about 2 inches in length. Joined to this tube by a rubber connection is a piece of glass tubing, B, of about the same bore, bent into a U; and joined in the same way to the free end of the U-bend is the constricted end of a straight tube C of about ½ to ¾-inch diameter. The whole thus forms a U-tube with a wide and a narrow branch and having a tap at the bottom of the wide branch; it is held as low as possible on a retort stand, the narrow branch by a clamp, and the wide one, most conveniently, by a clamp ring with a piece cut out of it, so that the narrow portion just above the tap can be slipped through the opening. Above the electrolysis vessel, held by a clamp, is a small parallel-sided separating funnel, D, the stem of which has been cut down to about 2 inches; joined to this stem by a rubber connection is the "mercury-jet tube," E, which is made as follows:

A side-arm is sealed into a piece of thick-walled capillary tubing and is bent round parallel to the main tube; about ¾ inch away from the seal on both sides the two arms of the main tube are bent round parallel to their original direction (and to the side-tube); we thus have a flattened loop, from the middle arm of which projects a side-tube bent parallel to one of the arms. The direction in which the side-tube points is the upper end of the tube; the lower end of the main tube is bent again at right angles about ¼ inch from the tip, and the bore of this tip is constricted by heating in a flame, the bore of the constricted portion being slightly less in diameter than that of a medium-sized pin; it is necessary that the bore of this jet should not be too large, otherwise the air-lift will not function properly. The upper end of the mercury-jet tube (*not* the side-tube) is attached by the rubber connection to the separating funnel; the lower end hangs free about halfway down the electrolysis vessel (or perhaps not quite so low) in such a way that the jet, whilst kept as near as may be to the wall of the vessel, points across it a little to one side. The object of this arrangement is to give the maximum length of unbroken mercury thread, whilst ensuring that the electrolyte is caused to rotate. Above the separating funnel, and also held by a clamp, is a second and larger one, F, of the same shape, the stem of which, passing right to the bottom of the smaller funnel, is terminated by a small U-tube made of narrow glass tubing, G, attached to the stem by a rubber connection and having the effect of the tip of the stem being turned up parallel to itself; the length of the turned-up portion should be about ¾ inch. The function of these two separating funnels is, the lower to act as a reservoir of mercury, and the upper to contain the purifying solution and to receive the returned mercury; the object of the turned-up end of the upper funnel is to prevent the purifying solution running into the reservoir and thence into the electrolyte if, for any reason (*e.g.* the pump ceasing to work), the reservoir becomes empty; the turned-up end is made detachable, so that the purifying solution may be run out and analysed at the end of the electrolysis. The mouth of the top funnel is closed by a rubber stopper with two holes; one





Mercury-jet tube.

carrying a tube, H, bent at right angles, the end of which, inside the funnel, is drawn out to a jet, the other a narrow tube, J, bent into a U-shape, so that the external arm points downward immediately above the wide tube connected with the bottom of the electrolysis vessel. The right-angled tube has a hole, K, blown in it about ½ inch above the jet and the same distance from the stopper; the hole is placed facing the wall of the funnel (*i.e.* towards the inner side of the angle); the free end of the tube is connected through a trap-bottle, L, with a filter-pump or other source of suction. To the free end of the downward pointing U-shaped tube is attached, by a rubber connection, a length of straight narrow tubing, M, passing inside the wide tube connected with the bottom of the electrolysis vessel and terminating in a jet, N, just above the level of the tap of that vessel. It is desirable to have this straight tube in two parts connected by a length of not too tightly fitting rubber tube, O, in order to facilitate adjustment of the level of the jet on which depends the level of the mercury in the electrolysis vessel; with this solitary exception, all joints of the apparatus which are held together by rubber should be pressed together as closely as possible, to avoid action of the mercury on the rubber. A general principle to be followed in setting up the apparatus is to eliminate waste height, so far as can be done, so as to make the work of the air-stream in lifting the mercury as light as possible. The complete apparatus can conveniently be held on one retort stand.

SETTING THE APPARATUS IN ACTION.—The taps of the two separating funnels, D and F, are closed, that of the electrolysis vessel, A, fully opened; the purifying solution is poured into the top funnel, F, and the stopper with its attachments replaced. The required amount of mercury (usually about 50 ml.) is poured into the electrolysis vessel, A, and the pump is turned on; this causes the mercury to be drawn up into the top separating funnel until the jet, N, at the bottom of the return tube, M, is free; the tap of the top separating funnel, F, is now fully opened, allowing the mercury to flow into the mercury reservoir funnel, D. If the height of the jet of the return tube has been properly adjusted, the mercury should now be just above the tap of the electrolysis vessel, A, the mercury reservoir funnel, D, should contain dry mercury, and the top funnel, F, and part of its stem should contain the purifying solution. The electrolyte is next poured into the electrolysis vessel, A, and the tap of the mercury reservoir, D, cautiously turned on (the pump being left running). As the tap is slowly opened the following phenomena occur: first the mercury runs down through the mercury-jet tube, E, and out of the orifice; as it does so air is drawn in through the side-tube, and consequently the mercury is projected from the orifice in spurts. As the tap is further opened the suction of air ceases, and the mercury settles down to a steady stream projected right across the vessel and striking the opposite wall; at the same time the mercury starts to rise in the side-tube, and, if the tap is too much opened, it is projected out of the top. The side-tube therefore acts as a manometer indicating the flow of the mercury, and the tap should be adjusted to keep ¼ to ½ inch of mercury in it. When the tap is opened the mercury flowing into the electrolysis vessel causes a rise in level round the jet, N, of the return tube, and consequently the air-lift comes into operation, the mercury being thrown in globules into the purifying solution in the top funnel, F. If the orifice of the mercury-jet tube, E, is too large, the flow of mercury becomes more than the air-lift can deal with; consequently mercury rises above the level of the jet of the return tube; the pressure, taking the way of least resistance, drives the mercury, followed by a rush of air, out of the mercury reservoir, D, into the top funnel, F. If this should happen, the taps of both funnels must be closed until the excess of mercury has been dealt with and the cause of the mishap eliminated, after which, first the tap of the top funnel, F, is fully opened and then that of the mercury reservoir, D, slowly opened as before. Electrical connection with the mercury jet is made through a 4-inch length of thin platinum wire pushed down the side-tube; finally the anode, Q, is placed in position. The anode consists of another 4-inch length of thin platinum wire, Q, bent double and having the free ends connected with the source of current; the platinum wire is sealed into a glass tube, P, leaving a length of about ½ inch of loop exposed; this anode is lowered gradually into the electrolyte until the desired current is obtained. In this way the anode current density is at a maximum, which, as was pointed out above, is what is required for many analytical operations. Set up thus, the apparatus should run without a hitch throughout the electrolysis; if it is desired to shut it off, turning the tap of the mercury reservoir, D, and stopping the pump are all that are required, but before restarting, the tap of the top funnel, F, must also be closed. It is desirable to have an ammeter in the electrical circuit; 0·5 to 0·8 amp. seems to be the best current at which to work. In disconnecting at the close of the electrolysis, if it is desired to analyse the purifying solution, it is necessary to draw this completely back into the top funnel, and this can readily be achieved by disconnecting the pump momentarily; this results in the mercury rising and blocking the jet, N, of the return tube, and, when the pump is reconnected, the suction draws the mercury up out of the reservoir, forcing the solution before it. The taps are now shut off and the apparatus dismantled; if the small U-tube, G, at the end of the stem of the top funnel is disconnected, the mercury runs out of the stem, and after the remainder of the mercury has been separated, the solution can be removed. The constitution of the purifying solution at present remains a problem; it is not always easy to dissolve metals out of mercury, but, for at least one metal (manganese), the problem has been satisfactorily solved. It is to be noted that the presence of any notable amount of ammonium salt in the electrolyte is to be avoided on account of the viscosity produced in the mercury, presumably owing to the formation of ammonium amalgam, and consequent hindrance of the flow of the mercury along the tubes.

I hope later to submit the results of studies of various separations carried out with the apparatus.

The Determination of Traces of Thallium in Presence of Other Metals

By L. A. HADDOCK, M.Sc., A.I.C.

THALLIUM has a limited use in medicine, and an increasing use in insecticides and rodenticides, so that it is important, in view of its very toxic nature, that methods should be available for its determination in traces. The green line, actually a triplet, at $535{\cdot}07 m\mu$ will detect at least $0{\cdot}002\gamma$, but it is desirable to have a chemical, apart from a spectrographic method, for measuring traces of thallium.

No true colour reactions capable of detecting traces appear to have been described, so that most chemical methods for the detection are indirect.

The dark brown colour, due to thallous sulphide, may be readily obtained in alkaline solutions of a thallous salt by adding a solution of sodium sulphide. The colour is produced in the presence of potassium cyanide, and in this respect resembles the colours produced by traces of lead or bismuth. Stich[1] finds that 1γ of thallium in 5 ml. of solution may be detected in this manner. However, since lead is itself so widely distributed in small amounts, it could never be assumed that the colour produced was not due, either wholly or in part, to this metal.

Pavelka and North[2] describe a nephelometric method for determining 20 to 100γ of thallium per ml. by adding a solution of phosphomolybdic acid to a solution of the thallous salt rendered faintly acid with nitric acid. Bismuth may be present to the extent of thirty times, or lead fifty times, the thallium-content, without interfering. However, salts of mercury, alkali metals and ammonia interfere, so that this method, again, is somewhat limited in scope.

A reaction which is available for the determination of thallium salts involves the reduction of thallic chloride by potassium iodide, whereby free iodine is liberated and constitutes a measure of the thallium present. This reaction may be used for quantities of thallium down to 500γ, as shown by Shaw.[3]

The method would obviously be open to considerable interference from traces of iron or copper, and it is necessary to isolate the thallium from these metals prior to its determination. Shaw effects this to some extent by obtaining the thallium in the form of thallic chloride. This is extracted from the aqueous solution with ether, in which it is quite soluble. Traces of ferric chloride are, of course, extracted at the same time, and this is probably the reason why his control experiments on thallium-free material show an apparent figure of 10 to 20γ of thallium as a blank.

During these experiments it was found, as described under bismuth,[4] that a chloroform solution of diphenylthiocarbazone would, under certain conditions, completely remove as much as 1 mg. of thallium from an aqueous solution. Thus, the possibility of the practical separation of the metal from most other elements, except lead and bismuth, seemed to be realised.

It now became necessary to find a method for the determination of very minute amounts of thallium, preferably in the presence of traces of lead or bismuth (which are also extracted), in order to show that the metal could be quantitatively separated, using diphenylthiocarbazone. Shaw (*loc. cit.*)[3] evaporates his ethereal solution of thallic chloride to dryness, destroys any organic matter in the residue by treatment with sulphuric and nitric acids, dissolves the residue in water, and oxidises the thallium in the solution by boiling with a solution containing bromine, sodium phosphate and hydrochloric acid. After all the bromine has been expelled, potassium iodide is added to the cooled solution, and the liberated iodine is extracted by shaking with carbon disulphide. The sodium phosphate in the oxidising solution tends to prevent liberation of iodine by traces of iron. The violet colour of the carbon disulphide solution is measured in the wedge of a Hellige Universal Colorimeter, which has been standardised against known amounts of thallium treated by this process.

Shaw stated that the method, originally used for quantities of thallium not less than 500γ, could be modified to deal with 50 to 500γ by using smaller volumes of solutions. Carbon disulphide is, however, an unpleasant solvent to use, so that, in making determinations in the range 0 to 200γ of thallium, it was decided to try the possibilities of the iodine-starch colour applied to Shaw's process, conducted on certain modified lines, necessary in dealing with such minute amounts.

THE QUANTITATIVE APPLICATION OF THE STARCH-IODINE COLOUR.—Shaw showed that the oxidation of the potassium iodide by the thallic chloride was fully quantitative, so that the liberated iodine was a true measure of the thallium present. The use of starch as a suitable measure of traces of free iodine has, however, been the subject of some dispute. Turner[5] found starch satisfactory for quantities of 0·5 to 5γ of iodine. Nichols[6] noted the retarding action of salts on the colour, as also did Reith.[7] Sah[8] recommends 4 to 12γ of iodine per ml. as the optimum concentration. He notes the influence of varying concentrations of potassium iodide used, and also the effect of reducing substances in the starch solution.

It seems necessary, if accurate results are to be obtained, that the starch-iodine colour should be produced under strictly comparable conditions as regards order and time of mixing of reagents, concentration of salts and temperature of solutions.

DETERMINATION OF THALLIUM BY MEANS OF THE STARCH-IODINE COLOUR.—When examined in a tintometer of the Lovibond type the starch-iodine colour was found to consist entirely of blue. On measuring the colour of a solution in a 1-cm. cell, and plotting a graph, the "blue units" and thallium-content were found to be proportional. This proved that the colour could be used as a true measure of the thallium present.

The tintometer was obviously not so accurate as a colorimeter, especially with quantities of thallium less than 100γ, but it was useful for rapid work when it was not possible to prepare a series of standards for each determination.

Owing to the sensitivity of the starch-iodine colour to the presence of various salts, etc., the colours recorded in terms of blue units are applicable only when prepared strictly according to the method described. If any one of the conditions is altered the proportionality between thallium-content and blue units may be altered.

Preparation of the Standard Thallium Solution.—Pure thallous nitrate of commerce was recrystallised from water, and the crystals were dried at 100° C. The salt was assayed gravimetrically as chromate according to the method of Moser and Brukl,[9] and 100·0 per cent. $TlNO_3$ was indicated. From this salt a solution containing 0·1 per cent. of thallium was prepared. From this solution a dilute solution was prepared freshly as required by diluting 10 ml. to a litre. One ml. of this dilute solution contained 10γ of thallium.

Method.—The required amount of standard thallium solution was added from a micro-pipette to about 40 ml. of a solution containing 0·5 g. of potassium cyanide and 0·5 g. of ammonium citrate. The thallium was extracted by vigorously shaking this solution with four portions of 15 ml. of a 0·1 per cent. solution of diphenylthiocarbazone in chloroform. Each extract was washed with 20 ml. of water, and the bulked chloroform extracts were evaporated to dryness in a 100-ml. Pyrex micro-Kjeldahl flask. One ml. of concentrated sulphuric acid was added to the residue, and the solution was heated over a micro-burner. The destruction of the organic matter was accelerated by dropping 30 per cent. hydrogen peroxide into the hot acid.

After the acid had become colourless, the solution was cooled and then washed into a 250-ml. beaker-flask with 20 ml. of water. One g. of ammonium chloride was added, followed by 25 ml. of special bromine reagent. The solution was boiled at such a rate that it became just colourless at the end of three minutes, and it was then rapidly cooled to 18° C. The volume of the solution was adjusted to 35 ml. after being transferred to a graduated 50-ml. stoppered cylinder. Five drops of a 25 per cent. solution of phenol in glacial acetic acid were added, and the solution was shaken and allowed to stand for three minutes. At the end of this time 5 ml. of a fresh 0·2 per cent. solution of iodate-free potassium iodide solution were added, and 1 ml. of starch-glycerol solution. The mixture was shaken and allowed to stand for exactly five minutes, the temperature being still approximately 18° C.

At this point a colorimeter should be used for very accurate work for measuring the blue colour produced, but, since it was desired to see how far the blue colour was proportional to the thallium present, the colour was measured in a 1-cm. all-glass cell in a Lovibond tintometer. The following results were obtained:

Thallium present in γ	0	10	20	30	40	50	70	90	100	130	150	175	200
Colour in blue units	0	0·4	0·7	1·0	1·3	1·6	2·1	2·7	3·2	4·0	4·6	5·3	6·0

A control experiment on the reagents used, which were all of A.R. quality whenever possible, showed no blue colour.

Preparation of Bromine Reagent.—One hundred g. of disodium hydrogen phosphate were dissolved in 900 ml. of freshly-prepared bromine water, and to this solution were added 100 ml. of concentrated hydrochloric acid.

Preparation of Starch-glycerin Solution.—Ten g. of soluble starch were made into a paste with 50 ml. of water, and this solution was added, with constant stirring, to 450 ml. of boiling water; 500 ml. of glycerin were added, and the solution was stirred and boiled gently for five minutes. After cooling, the volume was adjusted to one litre. When stored in amber bottles the solution could be kept for several months without deterioration. The soluble starch used for this solution should be examined for the presence of reducing sugars. If traces are present they may be washed out with cold water, but it is usually easy to obtain pure specimens commercially.

Notes on the Method.—The use of potassium cyanide and ammonium citrate in the aqueous solution used for the standards was necessary in order to prevent interference from heavy metals present in the diphenylthiocarbazone. On destroying some of the commercial substance with sulphuric acid and hydrogen peroxide, distinct traces of iron were obtained in the residue. This iron tended to pass through the various stages of the process and produce a fictitious blank of about 20 to 30γ of thallium, unless the above precautions were taken.

The thallium must be present in the thallous condition. Tervalent thallium does not react with diphenylthiocarbazone, but may be easily reduced to the univalent state by sulphur dioxide. This fact may be of use in separating thallium from traces of lead and bismuth, which also react with the reagent.

The addition of ammonium chloride to the dilute sulphuric acid solution is necessary in order to counteract the effect of this acid. Čůta[10] notes that bromine will oxidise thallium in presence of hydrochloric or hydrobromic acid, but not of sulphuric, phosphoric or perchloric acid. The bromine reagent used contains sufficient hydrochloric acid for the oxidation to be successful. The presence of phosphate helps to reduce any tendency towards interference by traces of iron. A control experiment on the reagents used, however, should always be carried out.

The rate at which the bromine is evolved depends on the rate of boiling. The time of boiling should not be excessive, as the thallium tends to become reduced again after the bromine has disappeared. By using a wide-mouthed flask, such as a beaker-flask, and with fairly brisk ebullition, the bromine may just be expelled in three minutes. A stop-watch may be used advantageously for the time measurements in the method.

The solution of phenol removed any minute trace of bromine which might remain in the solution, but did not affect the final colour. Three minutes' standing permits this reaction, if any, to be completed.

The colour is measured exactly five minutes after adding the potassium iodide and starch solutions. This is purely an arbitrary time-limit, but the colour tends to be somewhat stabilised after a few minutes. The colour increases on standing, as is shown below.

Time of standing Minutes	Colour Blue units
1	1·6
5	3·0
10	3·3
30	6·0

Application of the Method.—Metallic salts were dissolved in water, and a slight excess of solid potassium cyanide was added, together with sufficient ammonia, if necessary, to render the solution faintly ammoniacal. In the presence of iron or manganese up to about 0·5 g., 5 g. of citric acid were also added, followed by a slight excess of ammonia before the addition of the cyanide. The thallium, in the reduced state, was then extracted with the diphenylthiocarbazone solution as in the preparation of the standards.

It was found that the thallium was easily extracted from solutions containing alkali metals, alkaline earth metals, magnesium, aluminium, copper, iron, chromium, silver and some other metals.

Large quantities (of the order of 1 g.) of nickel, mercury and zinc, seemed to retard the extraction of the thallium, so that low results were obtained. In these specific cases about 0·1 g. of the metal was the upper working limit. Thallium evidently differs from lead and bismuth in this respect, although Allport and Skrimshire[11] note that considerable quantities of cobalt or nickel tend to retard the extraction of lead. Even six extractions with diphenylthiocarbazone did not completely remove 80γ of thallium from 0·5 g. of nickel, although they did so from 0·1 g.

Manganese tends to be carried through the process in minute traces and causes high results, owing to its oxidation by the bromine and subsequent reaction with the potassium iodide. For this reason, when a considerable amount of manganese is present, it is necessary to make a second extraction on the sulphuric acid solution produced by destruction of the diphenylthiocarbazone. Copper, which if carried through the process would also cause much interference, does not seem to have this effect. A second extraction is also necessary in the presence of considerable amounts of tin.

Sulphates, chlorides, phosphates and nitrates seem to cause no trouble in the preliminary extraction. This must always be carried out, even in the presence of a neutral substance such as sodium chloride, as it is not possible to be sure how the presence of such salts may affect the final starch-iodine colour.

The following are some typical results obtained with substances which did not interfere in the process:

Substance	Quantity g.	Thallium added γ	Thallium found γ	Notes
Copper	0·5	100	100	
Do.	1	20	21	
Do.	1	60	63	
Silver	1	30	28	
Iron (ferric)	0·5	100	105	
Do.	0·5	40	43	
Potash alum	2	60	63	Used 5 g. of citric acid as for Fe
Chromium	0·5	15	13	Cr present as $Cr_2(SO_4)_3$. Used citric acid
Antimony	0·5	25	27	Citric acid added as for Fe
Sodium chloride	5	70	68	
Potassium sulphate	5	30	33	
Ammonium nitrate	5	50	47	
Magnesium	1	30	28	
Sodium phosphate	2	60	64	
Calcium	1	100	105	
Strontium	1	45	48	
Cadmium	1	10	13	

In the presence of nickel, zinc or mercury, results were obtained which might be 50 per cent. low, if the concentration of the metal in the original aqueous solution was greater than about 0·1 g. in 50 ml.

Substance	Quantity	Thallium added	Thallium found	Notes
	g.	γ	γ	
Manganese ..	0·5	70	75	Double extraction
Do.	0·5	80	84	
Tin	0·5	30	32	Citric acid used and a double extraction
Mercury	0·1	50	47	0·1 g. upper limit
Zinc	0·1	90	85	Do.
Do.	0·1	70	67	
Nickel	0·1	80	76	Do.
Do.	0·1	30	29	Six extractions

EXAMINATION OF ORGANIC MATTER.—As with lead, ignition, even at low temperatures, is likely to lead to losses of thallium, so that destruction of the organic matter by wet oxidation is indicated. On 10-g. samples of meat, to which 30 and 100γ of thallium had been added, 28 and 95γ, respectively, were recovered by the above process, after oxidation of the organic matter with sulphuric and nitric acids.

NOTES ON SOME POSSIBLE REACTIONS FOR THALLIUM.—Various attempts were made during these experiments to find methods of measuring the isolated thallium other than that depending on the reaction with potassium iodide, but without success. The colour of thallic hydroxide is not perceptible in dilute solution, so that 1γ of thallium per ml. cannot be observed when present as thallic hydroxide.

Fifty γ of thallic chloride in 50 ml. of solution did not oxidise a solution of diphenylamine.

In the thallous condition thallium may be differentiated from lead by the action of sodium sulphite. Lead at a concentration of 10γ per ml. rapidly gives a distinct turbidity in an alkaline solution containing a sulphite. Thallium, when present to the extent of as much as 1000γ per ml., gives no turbidity.

SUMMARY.—A method has been described for the determination of about 5 to 200γ of thallium in the presence of 1 g. of many metals and their salts. Lead and bismuth interfere if present in quantities greater than about 0·5 mg., owing to their iodides being coloured, and mercury, nickel and zinc should not be present in quantities greater than 0·1 g.

I am indebted to Dr. A. M. Ward for his interest in this work.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF ZINC IN WATER BY MEANS OF SODIUM DIETHYLDITHIOCARBAMATE

THE dialkyl-dithiocarbamates were introduced by Delépine (*Bull. Soc. Chim.*, 1908, (iv), **3**, 652; Abst., *J. Chem. Soc.*, 1908, ii, 633) as reagents for copper and iron. Subsequently Callan and Henderson (ANALYST, 1929, **54**, 650) showed that sodium diethyldithiocarbamate was the most sensitive reagent for copper. They also pointed out that dilute solutions of many metallic salts (about 1 to 20 parts per million of the metal) gave a white turbidity or opalescence, but that barium, calcium and magnesium did not. They showed how iron and lead could be removed by the use of ammonia solution (*cf.* ANALYST, 1932, **57**, 495); but with zinc, the addition of 2 to 5 ml. of 0·880 ammonia per 100 ml. prevents interference with the copper reaction, provided the zinc present does not exceed 0·1 g. per 100 ml. (*i.e.* 1000 times the maximum amount of copper for which the method is suitable).

In the examination of a sample of water* from a well near Dartmoor, about three years ago, it appeared of interest to test for copper. On adding the reagent to the untreated sample a dense turbidity was immediately produced. A similar addition to Plymouth tap water gave no such result, nor did a number of other water supplies; even sea water gave no opalescence. The presence of lead was suspected, but was negatived. The turbidity, if due to lead, would not disappear upon addition of ammonia solution. It was finally concluded that the turbidity was due to zinc, the presence of which was quite unexpected. It appeared that the water had been pumped up into a new galvanised iron tank.

The turbidimetric estimation of the amount present proved simple. A stock solution of *N*/100 zinc sulphate was diluted suitably. The reagent was made up in 0·1 per cent. aqueous solution. On adding 10 ml. of reagent to 100 ml. of the sample and of standards, in Nessler tubes, it was found that the sample contained about 5 parts per million of zinc, which is well inside the upper limit of concentration for which the comparison is suitable. Even a standard solution containing 33 p.p.m. of zinc remained turbid and showed no settling two days after the addition of the reagent.

A sample of water from an old galvanised iron tank supplied with Plymouth tap water showed a turbidity corresponding to slightly less than 0·6 p.p.m. of zinc, whereas the Plymouth tap water, direct from the mains tap, showed a very faint turbidity (between 0·1 and 0·06 p.p.m. of zinc)—probably including and largely due to iron. Water from an old lead tank, also supplied with Plymouth tap water, gave results identical with that from the mains tap. Water from the Antony estate supply gave 2 to 3 p.p.m. of zinc, though three years ago none could be found. In the interval an additional supply, worked by a ram, had been included.

As regards the limit of delicacy of the method, a solution containing 0·065 p.p.m. of zinc gave the very faintest turbidity when compared with a blank after half an hour; the blank contained the reagent added to distilled water. On standing overnight the turbidity was more noticeable. No attempt was made to concentrate the metallic salt by extracting with chloroform or carbon tetrachloride, as is done for copper.

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* This water was of the usual type of Dartmoor waters, which are very soft and have a *p*H value of about 6·8, except when charged with carbon dioxide in excess of the equilibrium value, when they are more acid, but become alkaline (*p*H, 8·5) on boiling. They contain about 3 p.p.m. of silica, and have a very low phosphate-content (about 0·01 p.p.m. in winter to 0·001 p.p.m., as P_2O_5, in summer). The copper-content of the moorland streams may be under 0·001 p.p.m., but streams below the moor may contain as much as 0·005 p.p.m. The silica-content appears to be sufficient to prevent any serious action of the water on lead.

The method here described appears to be at least as delicate as the ferrocyanide method, which, according to Thresh and Beale (*Examination of Waters and Water Supplies*, London, 1925, p. 310), will detect with certainty 0·5 p.p.m. of zinc; as previously mentioned, the dithiocarbamate reagent will detect as little as 0·06 p.p.m. According to the authors quoted (*loc. cit.*, pp. 156–159), small amounts of zinc in water supplies are not injurious, but with an appreciable amount of zinc, "say 5 p.p.m., the water may be regarded as impure, but doubt could be expressed as to whether the water was unwholesome."

The colorimetric method using resorcinol (J. H. Yoe, *Photometric Chemical Analysis*, 1928, Vol. I, 396) is not as convenient as the method here described, since concentrations which give an immediate turbidity in the present test give the blue colour only on standing overnight. There is also interference from calcium.

SUMMARY.—Zinc may be estimated turbidimetrically in water supplies, in concentrations of from 0·05 to 25 p.p.m., using a 0·1 per cent. aqueous solution of sodium diethyldithiocarbamate. Unlike lead, the turbidity disappears in ammoniacal solution.

Iron may be removed as described by Callan and Henderson.

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MEASUREMENT OF THE SMALL VOLUMES OF NITROGEN OBTAINED BY THE MICRO-DUMAS METHOD

IN the micro-Dumas method for the determination of nitrogen in small quantities of organic material, there are certain points of difficulty inherent in the usual micro-azotometer employed to measure the volume of gas obtained.

These are connected with: (*a*) The initial calibration; (*b*) the unknown vapour pressure of the confining liquid, a solution of potassium hydroxide and potassium carbonate in continuously varying proportions; (*c*) the presence of a thin film of liquid on the walls of the azotometer, causing an appreciable apparent increase in the volume of nitrogen; (*d*) an increase in the pressure of the gas due to the surface tension of the confining liquid in the narrow graduated tube; the occasional formation of a fine persistent froth on the surface of the potash solution, rendering an accurate determination of the position of the meniscus impossible.

Of these, the first is usually surmounted by a calibration by weight with mercury, the nitrometer being in an inverted position. In this way the positive curve of the mercury meniscus simulates the negative one of the potash solution.

Although the extent to which (*b*), (*c*) and (*d*) affect the observed volume of the gas is not known, Pregl makes an empirical deduction of 2 per cent. from the observed volume of nitrogen to allow for these factors. He specially mentions (*c*). (*Die quantitative organische Mikroanalyse*, Berlin, 1930, p. 94.)

By the use of the apparatus shown in the diagram all these difficulties are avoided and increased accuracy obtained, as a measurement by volume is replaced by a measurement by weight.

Nitrogen evolved in the analysis is collected in the usual manner over potash solution in a modified nitrometer, fitted with a narrow jet sealed into the cup above the stopcock (Fig. 1).

Before any nitrogen is collected, the cup is filled with water, care being taken that all gas is expelled from the top of the nitrometer, the tap and the jet.

The gas volume is measured by means of the small flask, which has a total capacity of 7 ml., and is shown in the actual size in Fig. 2; it has a central neck sealed at the top with as flat an end as possible and with a millimetre scale etched throughout its length. A side-neck of the same diameter of tubing has a circular mark level with the top of the sealed neck. By grinding the open end of this side-tube smooth, without rounding it in the flame, the flask, when filled with water, can be inverted without the water escaping.

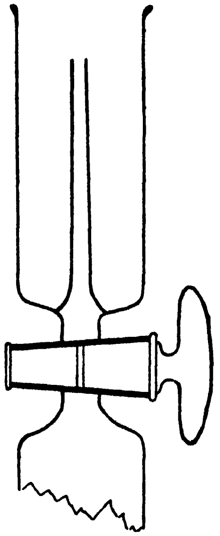

Fig. 1

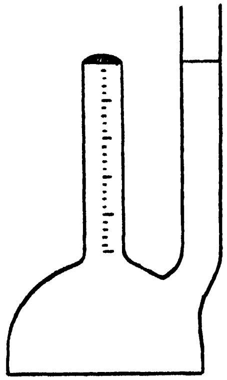

Fig. 2

At the end of the combustion, when all the nitrogen has been collected, the flask is filled with water and inverted over the jet in the cup at the top of the nitrometer. By raising the potash reservoir of the nitrometer and opening the tap, the nitrogen is expelled through the jet into the measuring flask, which is then removed and so tilted that the bubble of gas rises to the top of the closed central limb. Any traces of potash in the flask are then washed out by a stream of distilled water from a capillary tube inserted down the open neck, care being taken that no air bubbles are introduced. (It is necessary to use nitrogen-saturated water for this purpose and for filling the flask originally and also the nitrometer cup. A slight loss due to solution of nitrogen may otherwise occur.) The flask is then immersed to the top of the closed neck in water at a known temperature, and the water level in the open neck is adjusted to the mark, after which the flask is removed from the bath, dried and weighed to the nearest milligram. A similar weighing is made with the flask filled with water to the mark on the open neck. From the difference in weight the volume of nitrogen may be calculated accurately.

Corrections are applied for the vapour pressure of water and the difference between the water levels in the two limbs of the flask, indicated by the millimetre scale and mark respectively. A further small correction is necessary to allow for the weight of the nitrogen. No correction is necessary for surface tension, since the two limbs have the same diameter and the containing liquid is uniform throughout.

Summary.—An apparatus is described for the accurate determination of nitrogen in micro-Dumas combustions, characterised by measurement of a weight

instead of a volume and by avoiding some of the empirical features of present methods.

My thanks are due to Sir Robert Robertson for his encouragement and for permission to publish this work.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY OF ABERDEEN

REPORTS OF THE COUNTY ANALYST AND OFFICIAL AGRICULTURAL ANALYST FOR THE YEAR 1934

DURING the year the total number of samples examined under the Sale of Food and Drugs Act was 526, of which 271 were bought informally.

SULPHUR DIOXIDE IN MINCE.—Sulphur dioxide is permitted in mince during the months of June, July, August and September to the extent of 450 parts per million. One sample, sold in March, contained 580 parts per million, and was condemned.

BORIC ACID IN ESSENCE OF RENNET.—The authorities have no power to prohibit the presence of boric acid in rennet used for cheese-making, provided that the resulting cheese does not contain any boric acid. The amounts of boric acid found in two samples of such rennet, labelled "for cheese-making," were 2·10 and 1·03 per cent.

CHLORIDE OF LIME.—A sample labelled "Chloride of Lime" contained 18·72 per cent. of available chlorine. There is no standard for chloride of lime. Had the substance been labelled "Chlorinated Lime" it should have contained not less than 30 per cent. of available chlorine.

ACIDITY OF SULPHUR.—The acidity of the sample corresponded with 2·55 ml. of $N/10$ sodium hydroxide solution per 2 g. This is above the limit prescribed in the B.P., *viz.* 1 ml. of $N/10$ sodium hydroxide solution per 2 g.

COMPOUND FERTILISERS.—Of the 43 compound fertilisers analysed, nine were found to be below the guarantee in soluble phosphoric acid. In previous reports it has been pointed out that when these compound fertilisers were prepared they probably contained the amounts of soluble phosphoric acid guaranteed by the seller. Compound fertilisers, however, are known to contain, among other constituents, superphosphate (soluble phosphate) and ground mineral phosphate or other insoluble phosphatic compounds. Consequently, when a mixture of soluble phosphate and insoluble alkaline compounds has been made, a chemical action occurs, with the result that a certain proportion of soluble phosphoric acid is rendered insoluble. This reversion does not go on indefinitely; a balance is reached after a certain time, when the proportion of soluble phosphoric acid remains practically constant. Allowance for this reversion should be made by manufacturers when they give a guarantee of the amounts of soluble phosphoric acid in compound fertilisers. On the other hand, five of the compound fertilisers were above the guarantee in soluble phosphoric acid, showing that in these instances the manufacturer had allowed for the reversion in giving the guarantees. Whereas none of the samples was above or below the respective guarantee in nitrogen, ten were above, and none was below, the guarantees in potash. Only one sample of basic slag was sent in during the year in which the proportion of phosphoric acid found was 15·67 per cent., and the fineness of grinding 85·60 per cent. The usual figure for fineness of grinding in basic slags is 80 per cent. through the standard sieve.

WHITE FISH MEAL.—This is a feeding stuff now in common use, and is defined under the Act as "a product (containing not more than 6 per cent. of oil, and not more than 4 per cent. of salt) obtained by drying and grinding and otherwise treating waste of white fish, and to which no other matter has been added." In the following table the results of analyses of 6 samples disclose that the proportion of salt varied from 0·94 per cent. to 1·81 per cent., while the proportion of oil varied from 2·80 per cent. to 4·10 per cent.

Guarantee				Results of analyses			
Oil	Albuminoids	Salt	Phosphoric acid	Oil	Albuminoids	Salt	Phosphoric acid
3·50	64·00	2·00	8·00	3·12	56·32	0·94	6·53
4·00	64·00	2·75	8·50	4·10	64·12	1·35	7·61
4·00	64·00	2·75	8·50	3·71	63·26	1·58	8·22
4·00	60·00	3·00	9·00	3·32	63·05	1·81	9·51
3·75	64·00	2·75	8·50	3·73	66·44	1·24	7·59
4·00	63·00	2·00	7·00	2·80	62·93	1·35	8·09

CASTOR SEED IN FEEDING STUFFS.—The Fertilisers and Feeding Stuffs Standing Advisory Committee, after considering the complaints mentioned in my last year's Report, submitted its Fourth Report to the Minister of Agriculture, and the Department of Agriculture for Scotland in September. Dealing specially with castor seed, the Committee reported that, in view of the recognised poisonous character of castor seed, the presence of that seed in a feeding stuff should be deemed to be a deleterious ingredient in accordance with the terms of Section 7(2) of the Act, unless the contrary is proved. It is presumed that, in the case of castor seed, proof of its non-deleterious character would rest upon (i) any special treatment which the castor seed or the feeding stuff may have undergone to destroy the ricin of the castor seed; or (ii) the quantity of castor seed present in a particular feeding stuff being below that which would cause harm to cattle. There is no evidence that imported feeding stuffs undergo any special treatment to destroy the poisonous nature of any castor seed that may be present. It might, however, appear that a limit could readily be fixed for the permissible amount of castor seed in a feeding stuff below which the feeding stuff could be regarded as non-deleterious. This might be so if the castor seed gained entrance to the feeding stuff in such a manner as to be distributed regularly throughout it. It is, however, generally admitted that the contamination with castor seed is of an adventitious character arising from one or more of several causes, and that its distribution, when it occurs in a feeding stuff, is very uneven. As a result of this unequal distribution, a sample, taken in accordance with the Regulations from one part of a consignment, may be found to be free from castor seed, whilst a second sample drawn from the same consignment may show the presence of castor seed; and where two or more samples show the presence of castor seed the quantities present in the several samples will probably vary considerably. In these circumstances, the Committee reported that it was impracticable to prescribe a limit below which a feeding stuff containing castor seed can be regarded as non-deleterious. The Committee report that their intention is: (i) to give further consideration to the terms of the Fifth Schedule to the Act, with particular reference to whether any amendment is desirable in order to make it more effective in its application to the presence in feeding stuffs of poisonous substances coming within the class of the substances referred to in paragraph (*b*) of the Fifth Schedule; and (ii) to consider the question whether, in all the circumstances and having regard to the provisions of Section 2(4) and Section 26(4) of the Act in relation to statements of ingredients which take effect as warranties under the Act, it might be desirable to include in the methods of analysis of feeding stuffs prescribed in the Fertilisers and Feeding Stuffs Regulations of 1932 a method of analysis for the determination of castor seed or castor-seed husk in such foods.

J. F. TOCHER

ISLAND OF JERSEY

REPORT OF THE STATES ANALYST FOR THE YEAR 1934

THE total number of samples examined was 4475, of which 2802 were agricultural samples, and 839 were samples for the Public Health Committee.

FERTILISERS.—Generally speaking, fertiliser ingredients imported into Jersey during the last few years are no longer appreciably richer than they are guaranteed to be. The local fertiliser merchants had long been accustomed to expect the manures they mixed to be richer than the guarantees of the ingredients would justify.

STRENGTH OF SPIRITS IN JERSEY.—The legal minimum strength for brandy, gin, rum and whiskey is 70 degrees of proof spirit, and thus differs from the statutory English limits. A sample of "spirits" taken by the Impôt Officers proved to be 0·7 degree below the legal minimum strength. This was the first case under the "Law on the Sale and Consumption of Spirituous Liquors, 1932," and the publican was fined £5 by the Royal Court.

CIDER.—This is admitted duty-free, provided that no extraneous spirit is present. In suspicious cases the "original gravity" is determined.

MOISTURE IN TOBACCO.—The moisture in 74 samples of tobacco exported from Jersey was determined, as duty is not refunded on moisture in excess of 14 per cent.

CONDENSED MILK.—The Jersey law incorporates the English standards for the various grades of condensed milk. All samples were satisfactory.

ICE-CREAM.—Three samples (two imports, one of local make) of brands having very wide sale in the Island were analysed. They contained 13·99, 11·76 and 11·22 per cent. of butter-fat, and all were free from starch. The increase in the percentage of fat over that in the "ice-creams" made from milk and a form of custard powder, is to be attributed to the methods of "reconstituting" a "cream" from skimmed milk and unsalted butter, with a little gelatin as "stabiliser."

BORIC ACID ON FOWLS.—Eight fowls, received by post at various times from different vendors in the Irish Free State, were all found to have boric acid on them; they were condemned.

C. P. MONEY

THE ROYAL BOROUGH OF KENSINGTON

Report of the Public Analyst for the First Quarter, 1935

Of the 250 samples examined, 85 were bought informally.

Labelling of Cream.—A sample of cream had been sold in a glass bottle labelled "Guaranteed Pure Cream—direct from the West of England." The inference that any ordinary person would draw from such a statement is that the cream is a rich cream; in actual fact, however, it contained only 28 per cent. of fat, as against the 40 to 60 per cent. to be expected, and, moreover, contained a trace of tin. It had the general characteristics of a tinned cream, and the vendors have been asked for an explanation of the facts disclosed.

Cream Confectionery.—Of 11 samples of cream confectionery, 4 were reported against as containing a filling other than cream. Apart from prejudice to the purchaser, there is also the question of unfair competition in trade to be considered. For these reasons all confectioners within the Borough have recently been informed that they will render themselves liable to prosecution if they sell as cream confectionery any articles filled with cream substitutes. Already some firms have stopped the sale of this product under any name which includes the word "cream." One or two firms, however, have substituted the word "creamy" for "cream," and thus artfully contrive to evade prosecution while still practising the same deception.

Synthetic Acetic Acid and Wood Vinegar.—There is reason to believe that certain products sold as *wood* vinegar may not have been derived from the distillation of wood, but may have contained synthetic acetic acid. When the difficulty of securing sufficient quantities of the sample for the examination without raising the suspicion of the vendor have been overcome, the presence of synthetic acid in wood vinegar may be established, and in that event prosecutions will lie on account of false description.

Samples of artificial vinegar recently examined were labelled "Pure Wood Table Vinegar," apparently in an attempt to pass off the much cheaper artificial vinegar as being equal to malt vinegar for table use.

Report on Vinegar.—A report upon the subject of vinegar by the Medical Officer, Dr. Fenton, and myself, has been presented, dealing with the adulteration and mislabelling of vinegar.

"Spirit of Iodine."—An adulterated sample, sold as "spirit of iodine," was prepared wholly or partly with mineralised methylated spirit, although it was stated on the label to be made with industrial methylated spirit. The use of mineralised spirit in medicine, and especially in iodine preparations, is objectionable, as it contains pyridine and methyl violet, both irritant and toxic substances. A particular objection to the use of this spirit in iodine preparations is that the acetone which it contains combines with iodine to form an irritant compound.

Solution of Iodine.—An adulterated sample sold as "solution of iodine" contained: Iodine, 0·5; potassium iodide, 0·3; oily matter having the characteristics of tar oils, 1·3; industrial methylated spirit, 43·5; and water, 54·4 per cent. It was therefore deficient in both iodine and potassium iodide to the extent of 80 per cent. and in alcohol to the extent of 50 per cent. of the quantities required by the B.P. for the *weak* solution of iodine. Rectified spirit, which should have been used, was replaced by industrial methylated spirit, and this fact was admitted on the label. The oily matter was probably derived from the incorporation of a disinfecting fluid, which is a foreign ingredient in solution of iodine.

F. W. Edwards

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

POWDERED GENTIAN CONTAINING NUTSHELLS

On April 13th a druggist was summoned at Wolverhampton for selling powdered gentian adulterated with powdered nutshells.

Mr. L. Gore, for the prosecution, said that whatever medicinal value the gentian might have had would have been more than counteracted by the 87 per cent. of powdered nutshells and husks, and the effect upon a disordered stomach would be very harmful.

Samples of pure gentian and of the adulterated article were handed to the magistrate, and evidence was given that a qualified pharmacist should be able to distinguish between them.

For the defence it was stated that the supply of gentian had been obtained in good faith from a Birmingham firm, and that that firm had bought it, also in good faith, from the importers. Five pounds of the gentian had been used in various veterinary preparations, and it was doubtful whether 1 lb. of the 7 lbs. of the original stock had been sold over the counter. The main use of powdered gentian was to give horses an appetite; a different preparation was used as medicine for human beings.

The Stipendiary Magistrate fined the defendant £2, with 13s. 6d. costs. He did not think that the defendant's position as a dispenser under the National Health Insurance would be affected, as the sale related only to a veterinary medicine.

QUESTION OF A STANDARD FOR "CHEMICAL FOOD"

On April 18th the Glasgow Stipendiary Magistrate (Mr. George Smith) gave his judgment in a case in which a firm had been charged under the Food and Drugs (Adulteration) Act, 1928, with selling chemical food not of the nature, substance, and quality demanded, in that it was deficient in ferrous phosphate to the extent of about 18 per cent.

The Stipendiary Magistrate said that the case for the prosecution was that an inspector under the Food and Drugs Act asked for chemical food and did not get chemical food as that commodity is recognised according to the British Pharmacopoeia. The defence was that, whilst the complainer did not get chemical food according to the British Pharmacopoeia standard, notice was given to him by the label on the bottle that he was not getting chemical food of that standard, but was getting something else. To that, however, the Medical Officer of Health replied that, although the purchaser received notice that the article was not of the British Pharmacopoeia standard, it was not even up to the standard it was represented to be. It was maintained, on behalf of the Medical Officer of Health, that that constituted a contravention of the Sale of Food and Drugs Act.

The Stipendiary Magistrate said that, the purchaser, having been notified that he was not getting chemical food of the standard asked for, but was getting something else, he would not hold that the respondents had contravened the Act. The "something else" the purchaser received was not what was demanded, but what he accepted in lieu of what he asked for.

The respondents were found not guilty.

EXCESS OF SULPHUR DIOXIDE IN EGG SUBSTITUTE

On April 26th, at Thames Police Court, two firms were prosecuted by the Stepney Borough Council for manufacturing for sale egg-substitute powder containing an excess of sulphur dioxide.

The certificate of the Public Analyst (Mr. D. Henville, F.I.C.) showed that the powders contained 176 and 216 parts sulphur dioxide per million, respectively. As the only constituent of the powder in which sulphur dioxide is allowed is the starch (which may contain 100 parts per million), and the powders contained 30·3 per cent. and 29·8 per cent. of starch, this would represent 5·8 and 7·25 times the amount of sulphur dioxide allowed in the powder, or an excess of 480 and 625 parts sulphur dioxide per million, respectively, in the starch.

As these figures appeared unusually high for starch, by courtesy of the firms concerned samples of all the ingredients used were obtained. These samples, under various fancy names, consisted of sodium phosphate and maize starch, sodium bicarbonate, acid calcium phosphate, rice starch, egg-yellow dye, and neutral calcium phosphate.

All of these were examined for sulphur dioxide and sulphates and all were satisfactory, with the exception of the neutral calcium phosphate, which was labelled "dryer." This substance is an unusual constituent of baking powder or egg-substitute powder, and from its name is presumably used to keep the mixture dry. This powder contained 10,560 parts sulphur dioxide per million and some sulphate, and was responsible for the sulphur dioxide in the egg substitute. Counsel for the defence stated that sulphur dioxide had been found in the "dryer" by their analyst, and that the firm supplying them on warranty with the "dryer" admitted that it had been examined for lead and arsenic, but not for sulphur dioxide.

The firms were fined £5 with £4 4s. costs and £5 with £3 3s. costs, respectively.

Ministry of Health

THE SUPERVISION OF MILK PASTEURISING PLANTS*

The conditions that must be fulfilled by any person selling milk as "Pasteurised" were clearly laid down in the Milk (Special Designations) Order of 1923 [made by the Minister of Health under Sec. 3 of the Milk and Dairies (Amendment) Act, 1933], which provides for the licensing of dealers selling such milk and for their supervision by the Licensing Authority. The definition of pasteurisation contained in this Order is simple, the substantial requirement being that the milk should be heated to 145°–150° F., and kept at that temperature for half an hour. Although pasteurisation on a large scale presents difficult technical problems, the conditions laid down in the Order can be, and are, daily fulfilled by many dairymen dealing with both large and small quantities of milk. At the same time there is no doubt that pasteurisation is often carried out inefficiently.

The Cattle Diseases Committee of the Economic Advisory Council, in their recent Report,† recommended that pasteurisation of milk should be permitted only in plants, the design of which has been officially approved, which have themselves been tested on erection to ensure that they conform to the approved design, and which are frequently inspected, during working, by an officer of the sanitary authority, who should apply prescribed tests and record the results at each visit.

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* Reports on Public Health and Medical Subjects, No. 77. By Sir Weldon Dalrymple-Champneys, Bt., M.D., F.R.C.P. H.M. Stationery Office. Issued May 17th, 1935. Price 1s. 3d. net.

† Cmd. 4591. H.M. Stationery Office, 1935.

Owing to there being little information available with regard to the actual appliances and processes of commercial pasteurisation, the officers of local authorities have found it difficult to fulfil their duties in this direction, and dairymen and others concerned have complained that different, and sometimes unreasonable, requirements are demanded in different districts. The present Report has been prepared with a view to giving this information in concise form, and it may be regarded as an authoritative work on the technical aspects of pasteurisation, and, as such, forms an indispensable handbook for the inspecting officers of all local authorities concerned.

The Report, which occupies 47 pages, has an Introduction summarising the objects of the Report, and referring to the common causes of failure to secure efficient pasteurisation. This is followed by sections on The Objects of Pasteurisation, The Legal Definition of Pasteurisation, Raw Milk Supply, and the Construction of Premises. Then comes a description of the Component Parts of a Pasteurising Plant, comprising: (i) Tipping tanks; (ii) milk pumps; (iii) heater; (iv) filter, (v) holder; (vi) temperature recorders; (vii) cooler, (viii) pipe lines; (ix) balancing tanks. The chief requirements to be satisfied in the construction and operation of these different parts are discussed, the principal methods of solving the various problems involved are outlined, and the chief causes of failure are considered in turn. No attempt is made to compare the relative merits of different makes of thermograph, but the requirements of a good thermograph are discussed.

Methods of heat treatment other than that defined in the Order are referred to only briefly for the sake of comparison.

Sections on Bottle Filling and Bottle Washing have been added, since these are important parts of the commercial distribution of pasteurised milk, and the final section deals with the importance of laboratory control.

There are also three appendices, on (A) In-bottle pasteurisation; (B) efficiency of small plants; and (C) thermophilic and thermoduric organisms.

Department of Scientific and Industrial Research

THE INVESTIGATION OF ATMOSPHERIC POLLUTION

Report and Observations in the Year Ending 31st March, 1934*

The present publication is on the same lines as the previous ones, being the 20th in succession. It embodies the Report of the Standing Conference to the Co-operating Bodies for the year 1933–1934, pp. 1–2; the Report of the Atmospheric Pollution Research Committee for the year ended 31st March, 1934, pp. 3–4; the Report of the Superintendent of Observations, pp. 5–43; Appendix I with Addendum, pp. 44–58; Appendix II, pp. 59–60; and the General Deposit Tables, pp. 61–108.

Sulphur Gases in Air.—The results of the trials of the lead peroxide method (Analyst, 1933, **58**, 284; 1934, **59**, 280) are such that the method has now been accepted as a standard one, and is particularly recommended where it is desired to maintain observations at a number of points in a particular neighbourhood without undue cost. It provides a measure of the "activity" of the gases during the previous month; the "activity" or rate of attack on exposed surfaces depends on other factors besides the concentration of the gases, so that this method is not intended to supersede the older recommended method. Appendix I is a report of the trials.

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* Published 8th April, 1935, pp. 108. Obtainable at Adastral House, Kingsway, W.C.2. Price 5s. net.

DAYLIGHT MEASUREMENT.—Work in co-operation with the makers of the instrument has been undertaken with a new type of apparatus which will be largely automatic. The light falls on a photo-electric cell, and the resulting current charges a condenser which, when the charge reaches a definite amount, discharges through a neon lamp, causing an ordinary four-figure counter to move forward one unit. Suitable filters may be used, so that visible or ultra-violet light may be measured.

OPTICAL INTENSITY OF SMOKE ISSUING FROM A CHIMNEY.—General results so far appear to indicate that the mean of a number of readings with the photo-electric instrument (ANALYST, **1934**, **59**, **280**) at quarter-minute intervals gives the true darkness of the smoke within 25 per cent., and this corresponds with a quarter of one Ringelmann number and is likely to be sufficiently good for most purposes.

MEASUREMENT OF ULTRA-VIOLET RADIATION BY THE ACETONE AND METHYLENE BLUE METHOD.—In using this method for measuring ultra-violet radiation it is now realised that a control glass tube is necessary. This should be 3 mm. in diameter, and any fading in this should be deducted from that in the quartz tube. The control is necessary because an aqueous solution of methylene blue is sensitive to the visible spectrum. Whilst some stations have used a control tube, others have not, and therefore some ambiguity has crept into the results, and some of the figures given in last year's Report are not strictly comparable. The figures given for Rotherham and Sheffield are quartz-tube figures, and those for Hull and Stirling quartz-tube minus glass-tube figures. A much greater difference between summer and winter figures at Stirling than at either Hull or Southport thus becomes apparent. The difference between summer and winter figures cannot be attributed to smoke pollution, but there should not be much difference between the radiation received during the same month at places comparatively close together. A comparison of the figures at three stations in Sheffield and two in Rotherham shows an almost uniformly higher amount of radiation received at one station (Oakwood Hall Sanatorium).

COMPARISON OF ATMOSPHERIC POLLUTION IN LONDON AND PHILADELPHIA.—Observations of deposit of impurity, pollution by sulphur, dust counts by means of the Owen's Dust Counter, and ultra-violet observations by means of methylene-blue tubes, at thirteen different stations in the City of Philadelphia during the months of February and March, are compared with similar results at ten stations in London for the same months, and it is seen that the level of pollution in Philadelphia is very much higher than in London. Attempts were made to correlate the Philadelphia figures with the daily deaths, but with inconclusive results, although there was some evidence that several days of dense fog were followed by increased respiratory deaths. For February and March the figures for (*a*) London and (*b*) Philadelphia were, respectively: Tar: (*a*) 18·24, 24, (*b*) 42·49, 49; carbonaceous matter not tar: (*a*) 140, 237; (*b*) 388, 605; insoluble ash: (*a*) 223, 439; (*b*) 628, 815; ash of soluble matter: (*a*) 207, 423; (*b*) 226, 359; total solids: (*a*) 721, 1390, (*b*) 1400, 2140.

RECORD OF OBSERVATIONS.—A few new deposit gauge stations have been started, and additional gauges have been installed at other stations, but Ravenscourt Park and Wolverhampton gauges developed faults and the figures had to be omitted. Additional automatic filters have been in use, and results are also recorded for the determination of sulphur in air by the colorimetric apparatus, and with lead peroxide candles for estimating the "activity" of the sulphur impurity. The maximum and minimum mean monthly deposits, as metric tons per sq.km. (conversion tables are given, and the figures also tabulated as English units), were: Tar: Burnley, 101, Dewsbury, Whitley, 2; other insoluble carbonaceous matter: Bradford Central, 367, Bradford North, 43; insoluble ash: Liverpool, Netherfield Road, 765; Garston (nr. Watford), 41; ash of soluble matter:

London, Golden Lane, 644; Leeds, Park Square, 53; total solids: London, Golden Lane, 2,106; Rothamsted, 278; Rainfall: Newcastle-on-Tyne, Town Moor, 70 mm., London, Southwark Park, 29. The figures for tar are not so good as last year; the improvement noted last year in carbonaceous matter other than tar is not so great; insoluble ash remains much the same, and a very definite improvement in soluble ash is shown. Whilst all the constituents of the insoluble deposit show less, and all those of the soluble matter greater, improvement than in the previous year, total solids show a greater improvement. There is again evidence of some direct relation between soluble deposit and rainfall, and the improvement noted is almost certainly due to the reduction in rainfall. The excessive tar deposit noted in recent years at Golden Lane has again increased, and a possible cause is suggested in the proximity to the gauge of a large number of chimneys. The measurements of *p*H values reveals a general tendency towards a more acid atmosphere during the winter months.

D. G. H.

International Commission for Uniform Methods of Sugar Analysis

BRITISH NATIONAL COMMITTEE REPORT*

THE following Report of work done for the Committee was approved at a meeting of the Committee held in London on March 15, 1935:—

At the eighth session of the International Commission for Uniform Methods of Sugar Analysis, held at Amsterdam in September, 1932, several questions of analysis were recommended for further study.

Two of these problems have now been investigated under the auspices of the British National Committee, *viz.*

(1) The error due to the volume of the lead precipitate in testing raw cane sugars for polarisation; and

(2) The estimation of reducing sugars in raw cane sugars.

Five samples of raw cane sugar sent periodically to a number of chemists have been polarised: (*a*) after clarification with lead subacetate solution (as prescribed by the International Commission, Third Session, Paris, 1900); and (*b*) after making up the sugar solution to volume followed by clarification with Horne's dry subacetate of lead. The results obtained are given in Table I.

These results show that the use of lead subacetate solution, prior to making the sugar solution to volume, gives a higher polarisation (0·06 to 0·09 per cent. for the sugars tested) than that obtained with dry lead subacetate, and they substantially confirm the work of F. W. Zerban and C. A. Gamble (*Facts About Sugar*, 1933, **28**, p. 180), who found that for Cuban sugars of 96° polarisation, wet clarification gives results about 0·14 per cent. higher than those obtained with dry clarification. These differences are, of course, due to the volume of the lead precipitate, the effect of which is eliminated when the sugar solution is made up to volume prior to clarification.

The International Commission at its Third Session, held in Paris in 1900, agreed that:—"As clarifying and decolorising reagents there may be used: subacetate of lead, prepared according to the Pharm.-Germ. (three parts by weight of acetate of lead, one part by weight of oxide of lead, ten parts by weight of water);

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* Reprinted from *The International Sugar Journal*, 1935, **37**, 180–187.

Scheibler's alumina cream, concentrated solution of alum," and lead subacetate solution has generally been used for this purpose.

If the term "polarisation" is defined in accordance with this ruling, the volume of the lead precipitate produced by lead subacetate solution cannot be said to cause an error. Further, raw cane sugars contain reducing sugars and other optically-active minor constituents, the net effect of which is to lower the polarisation. Lead subacetate precipitates part of the reducing sugars, but the net effect of the reducing sugars and other minor constituents left in solution after clarification is still negative and opposite in sense to the effect of the volume of the lead precipitate. In the case of raw cane sugars both the effect of the volume of the precipitate and that due to laevo-rotation of the minor constituents are rather small, and since they are opposite in sense, their net effect is in general negligible. With dry lead subacetate, the effect of the volume of the lead precipitate is eliminated, but not the effect due to laevo-rotation of the minor constituents.

TABLE I

No. of sample	Mean pol. with lead subacetate solution (*a*)	Vol. of lead subacetate sol. used ml.	Mean pol. with Horne's dry lead subacetate (*b*)	Wt. of Horne's dry lead sub-acetate used g.	Mean diff. between pols. (*a*)—(*b*)
47 (12 chemists)	97·90	—	97·82	—	0·08
48 (15 chemists)	95·27	max. 3·0	95·18	max. 1·5	0·09
		min. 0·75		min. 0·3	
		av. 1·7		av. 0·6	
49 (15 chemists)	98·11	max. 2·0	98·05	max. 0·5	0·06
		min. 0·25		min. 0·1	
		av. 1·2		av. 0·35	
50 (13 chemists)	96·47	max. 2·0	96·40	max. 2·0	0·07
		min. 0·5		min. 0·2	
		av. 1·15		av. 0·48	
51 (15 chemists)	98·42	max. 2·3	98·35	max. 0·5	0·07
		min. 0·5		min. 0·2	
		av. 1·2		av. 0·37	

TABLE II

	Percentage of reducing sugars			
Method	48	49	50	51
Lane and Eynon ..	1·58; 1·57	0·43; 0·40	0·59; 0·50	0·45; 0·37
	1·54; 1·54	0·40; 0·39	0·49; 0·48	0·36; 0·34
	1·54; 1·50	0·39; 0·38	0·46; 0·45	0·34; 0·33
	1·48; 1·46	0·37; 0·36	0·41; 0·41	0·32; 0·32
	1·43	0·36; 0·36	0·41; 0·40	0·32; 0·31
		0·34		0·30; 0·27
	Mean=1·52	Mean=0·38	Mean=0·46	Mean=0·34
Potassium iodide and starch	1·64	0·43	0·47	0·32
Main's pot method ..	1·55	0·37	0·46	0·32
Herzfeld	1·52	—	—	—
Wein	1·75	0·50	0·53	0·33
External indicator ..	1·57	0·44	0·60	0·41
Boiling-water method ..	—	0·30	0·39	0·30
Average of all determinations	1·55	0·39	0·47	0·34

The Committee therefore recommends that the use of lead subacetate solution for the clarification of sugar solutions prior to polarisation should be continued.

The amounts of lead subacetate used for clarification, both in solution and as the dry salt, by the different chemists varied rather widely; it is advisable to use the minimum quantity requisite for good clarification.

The percentages of reducing sugars in the samples were also determined, various methods of analysis being used. The results obtained are given in Table II.

Lane and Eynon's method, the potassium iodide and starch method, and Main's pot method, gave the most concordant results, the first-named being most often used. Lane and Eynon's method, or the amplification known as Main's pot method, or other modification based on the use of methylene blue as internal indicator, is recommended for general use.

United States Department of Agriculture

FOOD AND DRUG ADMINISTRATION

SERVICE AND REGULATORY ANNOUNCEMENTS

TEA NO. 9

STANDARDS UNDER THE TEA ACT

EFFECTIVE MAY 1, 1935

THE following standards prepared and submitted by the Board of Tea Experts are hereby fixed and established as standards under the Tea Act for the year beginning May 1, 1935, and ending April 30, 1936:

(1) Formosa Oolong.
(2) Formosa Black.
(3) Congou.
(4) Java (to be used for all fully fermented teas excepting China, Japan, Formosa).
(5) Japan Black.
(6) Japan Green.
(7) Japan Dust.
(8) Gunpowder (to be used for all China green teas).
(9) Scented Orange Pekoe.
(10) Canton Oolong (to be used for Scented Canton and all China Oolongs).

These standards apply to tea shipped from abroad on or after May 1, 1935. Tea shipped prior to May 1, 1935, will be governed by the standards which became effective May 1, 1934.

As standards are set this year for the fermented teas, Formosa Black and Japan Black, Regulation 20 under the Tea Act is hereby modified to omit the statement:

"Should Japans be made as fermented teas, they are to be examined in comparison with the Congou standard."

The Japan and Formosa fermented teas should be judged by their respective standards.

R. G. TUGWELL
Acting Secretary of Agriculture

WASHINGTON, D. C., *March* 25, 1935

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Essential Oils from Mushrooms. F. W. Freise. (*Perfumery and Ess. Oil Record*, 1935, **26**, 91–92.)—Fresh, well-developed individual specimens of the genera *Clitocybe*, *Cortinarius*, *Hydnum*, *Hygrophorus*, *Hypholoma*, *Lactarius*, *Pleurotus*, *Polyporus*, and *Psalliota* (urupês, orelha de páo, or "woodear") found in Brazil, gave the following analytical data (as percentages):—Nitrogenous substances, 1·68 to 2·82; fat, 0·31 to 0·55; nitrogen-free extractive, 3·33 to 4·72; crude fibre, 0·88 to 1·65; mineral residue, 0·92 to 1·63; moisture, 92·88 to 88·63; sulphur in mineral residues (as SO_3), 3·65 to 9·25. Well-dried mushrooms (10 per cent. of moisture) contained 4·0 to 4·5 per cent., 11 to 13, and 26·0 to 29·8 per cent. of substances soluble in ether, 70 per cent. alcohol, and hot water, respectively. Soon after the maximum dimensions of the fungus are reached autolysis occurs, and 80 to 82 per cent. of the material is converted into water, ammonia and carbon dioxide, the solid residue being mainly chitin and cellulosic matter. Most of the essential oils exist in glucosidal combination in the stem and caps, but a small proportion occurs combined in the wax-like outer surface of the cap. These oils differ in composition in the case of the *Cortinarius*, *Hydnum* and *Pleurotus* species, and oils in the former class, without exception, contain sulphur compounds. Steam-distillation yields 0·00125 to 0·035 per cent. of oil (*cf.* Aye, *Arch. Pharm.*, 1931, **269**, 246; *Apoth.-Ztg.*, 1932, **47**, 1027), but this is considered too drastic a method of separation. It is preferable to obtain the glucosides by careful evaporation under reduced pressure of an extract in water, but specific enzymes are required for hydrolysis, and these may be obtained from the plant by irrigation with water for several days, followed by extraction with glycerin, and precipitation of the extract with benzene. The material is dried over phosphorus pentoxide, and the enzymes of *Clitocybe*, *Hypholoma* and *Polyporus* were then obtained as a white powder (sp.gr. 0·950 to 1·110), which produced an opalescent, foaming, non-dialysable solution with water. They were not homogeneous, and acted rapidly on glucosides, cellulose, hemicellulose, starch and sugars. The maximum hydrolysis occurs at 35° to 42° C. and *p*H 6·2 to 6·6, and it proceeds without variation in energy throughout the period of decomposition. If the concentration of glucoside is less than 10 per cent. and foreign enzymes are absent, the essential oils are easily separated, since they are heavier than water. It is considered that the glucosides and enzymes occur in separate groups of cells, and that widely different types of reaction may be initiated according to the age and vitality of the fungus. No relation appears to exist between the constitution of the products of enzymic decomposition and the organic matter on which the fungi grow. The principal constituents of the oils are *Clitocybe* (*clavipes*) and *Cortinarius* (*var. spec.*), 82·5 to 86·2 per cent. of benzyl *iso*thiocyanate, with phenyl-hydroxy-acetonitrile; *Hydnum* (*cyathiforme*) and *Hygrophorus* (*sp.*), 75·8 to 81·3 per cent. of phenylethyl *iso*thiocyanate; *Polyporus* (*melanopus*), 88·85 per cent. of benzyl *iso*thiocyanate.

J. G.

Determination of the Diastatic Power of Malt by Potassium Ferricyanide Titration. F. W. Norris and W. A. Carter. (*J. Inst. Brewing*, 1935, **41**, 167–171.)—For the final titration of the starch conversion liquid obtained in the determination of the diastatic power of malt, Cole's method (Abst., ANALYST, 1933, **58**, 616) is recommended. This procedure gives a much sharper end-point than titration with Fehling solution in presence of methylene blue alone. The solutions required are: (i) 1·333 per cent. potassium ferricyanide solution, which keeps for some weeks when stored in a dark bottle away from the light; (ii) 2·5 *N* sodium hydroxide solution, standardised against hydrochloric acid solution in presence of methyl red; (iii) aqueous 1 per cent. methylene blue solution.

A preliminary titration is first carried out: 20 ml. of solution (i) and 5 ml. of solution (ii) are placed in a small conical flask, with a pinch of powdered pumice or broken porcelain. The liquid is heated to boiling on a wire gauze and the conversion solution is run in from a burette at the rate of 1 ml. every 15 seconds until the yellow colour diminishes in intensity. One drop of solution (iii) is then added from a tube drawn out to deliver 25 drops per ml. The titration is continued until the purple solution becomes colourless. For the final titration, a volume of the conversion liquid less by about 0·2 ml. than that used in the preliminary titration is run into the mixture of 20 ml. of (i) and 5 ml. of (ii) containing pumice. The liquid is heated to boiling (in not more than 2 minutes), and kept boiling steadily for 1 minute. The titration is completed, by adding the conversion liquid dropwise, in not more than a further 2 minutes. As the preliminary titre is usually smaller than the final one, about 0·5 ml. will be required for the completion. The times indicated should be closely adhered to, and the total time from the commencement of heating should not exceed 5 minutes. Shortly before the end-point is reached the purple colour of the liquid becomes very marked, and, within one or two drops of the end-point, changes to a delicate pink; after this, one or two additional drops render the solution colourless. The titration values thus obtained agree closely with those given by the standard method, so that the ordinary formula for Lintner value is applicable directly. T. H. P.

Comparative Composition and Colour of Commercial Tomato Juice. J. S. Mitchell. (*J. Assoc. Off. Agr. Chem.*, 1935, **18**, 128–135.)—Samples of tomato juice, packed in 1932, and produced in various parts of the United States, have been examined for composition and colour. Total solids were determined by drying 5-g. samples of the well-mixed juice, in covered aluminium dishes *in vacuo* at 70° C. overnight (usually for about 16 hours). The total solids were calculated as percentage by weight of the fresh juice. For the determination of soluble solids, 37·5 g. of the well-mixed juice were weighed into 250-ml. flasks, diluted to the mark with water, and thoroughly mixed. This mixture was then filtered. Twenty-ml. aliquot portions of the filtrate were dried *in vacuo* at 70° C. overnight. The weight of the residue of soluble solids was calculated as percentage by weight of the original juice. The salt-content of the same filtrate was determined by titrating 20-ml. portions with 0·1 *N* silver nitrate solution, with potassium chromate as an indicator. The results were again calculated to percentage by weight of the original juice. Again on the same filtrate, the total acid was determined by the titration of 20-ml. portions with 0·1 *N* sodium hydroxide solution, with phenolphthalein as an indicator. The total acid was calculated as citric acid and expressed as a percentage by weight of the original juice. The refractive index was determined on filtrates of the undiluted juice at 20° C., allowances of ±0·0001 being made for each degree above or below 20° C. Colour measurements were made by means of standard colour discs prepared and calibrated after the Munsell system (see also *A Practical Description of the Munsell Colour System,* Munsell Color Co., Baltimore, 1921; Nickerson, *U.S.Dept. Agr. Tech. Bull.*, 1929, **154**; and MacGillivray, *Purdue Univ. Agr. Expt. Sta. Bull.*, 1931, **350**). The method of MacGillivray consists in subtracting the chroma number from 13 and adding the result to the hue number. This method was used in expressing results. It was also found possible to calculate the total soluble solids from the refractive index by means of the formula:

$$\text{Total soluble solids} = (662{\cdot}25 \times n_{\mathrm{D}}) - 883{\cdot}18.$$

Determinations of the *p*H values were made by means of the glass electrode, the quinhydrone electrode, the hydrogen electrode, and colorimetrically by the standards of Michaelis, and also of La Motte. All five methods gave results in fairly good agreement, values varying from *p*H 3·8 to 4·38 for different samples. The following table gives the maximum, minimum and average values found for juice from the Western and the Eastern parts of the United States.

TOMATO JUICE SAMPLES

	Total solids Per Cent.	Total soluble solids Per Cent.	Refractive index n_{D}^{20}	Salt Per Cent.	Total acidity, as citric acid Per Cent.	Hue	Colour		Rating
							Chroma	Value	
From Western Unites States									
Average	6·74	6·19	1·3430	0·555	0·388	6·62	10·38	2·96	9·28
Maximum	8·31	7·71	1·3445	1·071	0·563	5·32	11·85	2·52	6·47
Minimum	5·28	4·85	1·3411	0·022	0·233	7·76	8·49	3·29	11·94
From Eastern United States									
Average	6·16	5·68	1·3423	0·687	0·383	6·98	9·92	3·02	10·09
Maximum	8·71	8·00	1·3464	1·059	0·496	6·05	11·29	2·44	8·33
Minimum	4·72	4·12	1·3396	0·000	0·269	8·15	7·21	3·32	12·38

S. G. S.

Determination of the Acid Value of Flour-fat for judging the Age of Flour. N. P. Kosmin and K. A. Alakrinskaja. (*Das Muhlenlaboratorium,* 1935, 5, 33–36.)—The most sensitive indication of the degree of freshness of flour is the magnitude of the acid value of the flour-fat, this being independent of the fat-content of the flour. The acid value of the fat is relatively constant for freshly-ground flours, varying only from 15 to 20 mg. of potassium hydroxide per 1 g. of fat. The theoretical maximum for this acid value is, on the average, 180 mg. of potassium hydroxide per 1 g. of fat. Thus, the acid value of the flour (by which the authors mean that of the fat) gives a measure of its age or degree of maturation, on which the consistence of the dough depends. Complete removal of the fat from flour is achieved only after extracting with ether for

8 hours in a Soxhlet extractor, but a sufficient quantity of the fat having the same acid value as the total fat is obtainable in a much shorter time. The procedure recommended is as follows: 20 g. of the flour are introduced, in a filter-paper thimble, into a weighed 350- to 400-ml. Erlenmeyer flask, to which 200 ml. of petroleum spirit (b.p. 80° C.) are then added. The flask is heated for an hour under a reflux condenser on a boiling water-bath, the thimble being then removed by means of tweezers and rinsed with 20 ml. of the petroleum spirit. The solvent is evaporated from the flask, which is dried in an oven at 75° to 80° C. for 2 hours, and weighed. The known quantity of fat is dissolved in 40 ml. of a 1 : 1-mixture of neutral alcohol and ether, and the solution titrated against 0·01 *N* potassium hydroxide, phenolphthalein (or, with a dark fat, thymolphthalein) being used as indicator. The values thus obtained agree well with those found by the usual method, in which the fat is first completely extracted.

The following results, expressed as mg. of potassium hydroxide per 1 g. of fat, were obtained with different flours: 100 per cent. extraction (2 samples) immediately after grinding, 14·5, 17·9; 75 per cent., 17·9 (just ground), 26·2 (after 8 days at room temperature); 85 per cent., 41·0 (25 days at room temperature), 92·4 (6 months at room temperature), 114·3 (45 days at 30° C.); 70 per cent. (all kept for 90 days at about 12° C.), 45·1, 51·2, 55·4, 55·6. T. H. P.

Component Glycerides of Piqui-a Fats. T. P. Hilditch and J. G. Rigg. (*J. Soc. Chem. Ind.*, 1935, **54**, 109–110T.)—Piqui-a (*Caryocar villosum*), a tree indigenous to Brazil, and cultivated to some extent in Malaya, has a fruit which contains fatty matter both in the mesocarp and in the kernel, and these fats bear a resemblance to palm oil in consistence and composition, and form one of the somewhat rare instances in which endosperm (or embryo) and fruit-coat fats from the same fruit are almost similar in composition. The fruit consists of about 74 per cent. of hard outer pericarp with one to 4 seeds, each surrounded by mesocarp (13 per cent. of fruit) containing about 47 per cent. of fat, inside of which is the shell (11 per cent.), enclosing the kernel (usually less than 2 per cent. of the fruit), containing 45 per cent. or more of fat. The general characteristics of the fats were (*a*) kernel, (*b*) fruit coat fat; saponification equivalent, (*a*) 284·0, (*b*) 281·6; iodine value, (*a*) 48·6, (*b*) 47·8; acid value, (*a*) 0·9, (*b*) 10·6; unsaponifiable matter, (*a*) 1·7; (*b*) 0·8 per cent., with iodine value, (*a*) 183, (*b*) 282. The mean mol. wt. of the mixed fatty acids was (*a*) 271·4, (*b*) 268·7; iodine value, (*a*) 50·0, (*b*) 50·0; setting point, (*a*) 48·5°, (*b*) 48·7° C. The composition of the mixed fatty acids was myristic, (*a*) 1·6, (*b*) 1·8; palmitic, (*a*) 50·7, (*b*) 47·3; stearic, (*a*) 0·8, (*b*) 1·7; oleic, (*a*) 43·7, (*b*) 47·3; linolic, (*a*) 3·2, (*b*) 1·9 per cent. (mol.). The average unsaturation of the fruit-coat fatty acids is slightly greater than that of the kernel fatty acids. The kernel-fat conforms to the usual seed-fat rule of even distribution of fatty acids throughout the glycerol molecules. The fruit-coat fat resembles the corresponding Sterculia fat (ANALYST, 1934, **59**, 632) in corresponding with the kernel-fat type of distribution, thus differing from palm oils. A portion of the fruit-coat fat was hydrogenated almost completely and systematically crystallised, and the fractions were examined. A partly hydrogenated fat was also analysed. The component glycerides (wt. percentages) of the original fat are given roughly as: tripalmitin 2; dipalmito-oleins 42; palmitodioleins 56 per cent. Both α- and β-palmitodioleins and α- and β-oleodipalmitins are probably present in appreciable quantity. D. G. H.

Koryan (Kaoliang) Oil. S. Ueno and R. Yamasaki. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 113–116B.)—Koryan corn (*Andropogon Sorghum* var. *vulgaris* Hack.), a very important product of Manchukow, from which an increasing amount of germ and shells are likely to be available as bye-products, yields 3·3 per cent. of a deep yellow oil with the following characteristics: Sp.gr. at 20°/4° C., 0·9260; n_D^{20}, 1·4655; saponification value, 187; iodine value (Wijs), 121; unsaponifiable matter, 8·6 per cent.; acid value, 18·5; saponification value of neutral oil free from unsaponifiable matter, 204; neutralisation value of mixed fatty acids, free from unsaponifiable matter, 210; iodine value of the unsaponifiable matter, 62·0. The composition of the unsaponifiable matter varied according to the solvent used, and with (*a*) ether and (*b*) benzene extraction was found to be, "takakibyl" alcohol, (*a*) 2, (*b*) 6; "koryanyl" alcohol, (*a*) 12, (*b*) 28; sitosterol, (*a*) 21·6, (*b*) 50; cetyl alcohol and $C_{30}H_{48}O_3$ (?), etc., (*a*) 63, (*b*) 15·6 per cent. This oil appears to be very suitable for the preparation of sitosterol, owing to the high proportion present, the ease of purification and the absence of other phytosterols. Three new alcohols were isolated from kaoliang oil: koryanyl alcohol ($C_{28}H_{58}O$), apparently the next higher alcohol to ibotaceryl alcohol, mol. wt. 410; takakibyl alcohol ($C_{44}H_{90}O$), m.p., 71 to 71·5° C., mol. wt. 634, iodine value 11·9; and an alcohol $C_{30}H_{48}O_3$ (?). D. G. H.

Fatty Substances of Japanese Shell-fish. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 118–120B.)—*Kumanokogai*.—This somewhat conical shell-fish, weighing 1·7–7·9 g., yielded, on extraction with ether, an acetone-insoluble, dark yellow-green viscous material (phosphatides) and a liquid acetone-soluble portion with solid in suspension. The fatty acids had m.p. 32·5 to 33·5° C., iodine value (Wijs) 153·4, ether-insoluble bromide 40·3 per cent. The unsaponifiable matter, after recrystallisation from methanol, consisted of long, white prismatic crystals, m.p. 145 to 146° C., giving no depression of m.p. when mixed with cholesterol, and an acetyl compound of m.p. 118 to 118·5°C. It is regarded as consisting chiefly of cholesterol, probably mixed with a small amount of conchasterol. *Shako*.—These very large shell-fish, weighing 345 to 783 g. each (3 specimens), gave an ethereal extract nearly all of which was soluble in acetone. The fatty acids had m.p. 42 to 43° C., iodine value 91·3, and ether-insoluble bromide 16·3 per cent. The proportion of highly unsaturated acids was small. The low iodine value, compared with that of the fatty acids of other shell-fish, was to be expected from the tropical origin of shako. The unsaponifiable matter was found to contain a new sterol, called "shakosterol," an isomer of cholesterol, giving an acetyl compound with high m.p., 156 to 157° C.

D. G. H.

Characteristics of Halibut-liver Oils. N. Evers and W. Smith. (*Pharm. J.*, 1935, **134**, 417.)—Analytical data for halibut-liver oil, which were scanty when the monograph in the B.P.C. 1934 was written, have now accumulated to an extent which makes it possible to prescribe more definite limits than previously. Analytical figures for this oil from known sources have already been given by Haines and Drummond (*J. Soc. Chem. Ind.*, 1934, **53**, 81T; Abst., ANALYST, 1934, **59**, 358; and *Brit. Med. J.*, 1933, i, 558), and also by the present authors (*Quart. J. Pharm. and Pharmacol.*, 1934, **7**, 482), while Lovern, Edisbury and Morton (*Biochem. J.*, 1933, **27**, 1461) have published figures for the vitamin-*A* content. The present paper gives the results of the analyses of 33 oils of known origin. All of these results are summarised in the table, which also indicates the extreme values obtained.

	Blue value	Vitamin *A* $E^{1\%}_{1cm.}$ 328$m\mu$	Sp.gr. 15·5/15·5°	Ref. ind. 40° C.	Iodine value	Saponification value	Unsaponifiable matter Per cent.
Evers and Smith	205–7100	6·8–144	0·922–0·9286	1·470–1·488	111–171 (R–K)	150–175	8·3–21·5
Haines and Drummond	650–8700	—	—	1·474–1·478	116–161 (R–K)	172–180	9·2–12·7
B.P.C.	400–3000	—	0·922–0·925	1·470–1·478	120–136 (Wijs)	170–180	8 –13
Lovern, Edisbury and Morton	60–7630	3·5–164	—	—	—	—	—

The Rosenmund-Kuhnhenn pyridine sulphate bromide method for determining iodine values (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154–159; Abst., ANALYST, 1934, **49**, 105) was found to give the most consistent results, and is recommended as a standard procedure for halibut-liver oil. S. G. S.

Colorimetric Micro-Determination of Morphine in Opium and its Preparations. J. A. Sanchez. (*J. Pharm. Chim.*, 1935, **21**, 366–376.)—The solutions required are: (i) Wavelet's reagent: 70 g. of recently calcined molybdic acid are dissolved in a solution of 140 g. of sodium carbonate and 20 g. of disodium phosphate in 500 ml. of water; 200 g. of tartaric acid are then dissolved in the solution, the whole being made up to 1 l. with water, and filtered after 24 hours. (ii) Morphine hydrochloride solution of 1 : 10000 strength. (iii) Ammonia solution of sp.gr. 0·980. To prepare a scale for comparison, ten similar test-tubes of colourless glass are charged with 1, 2 . . . . , 10 ml. of solution (ii), 1 ml. of (i), and 1 drop of nitric acid. After 10 minutes the liquids are mixed, diluted with water to give the same depth in all the tubes, and again mixed; 20 drops of (iii) are then mixed into each. The blue colours thus obtained reach their maximum intensity within a minute and remain unchanged for about 15 minutes. Of the solution to be tested, 1 ml. is made up to 100 ml. with water, 1 and 6 ml. respectively of this solution being transferred to two test-tubes and treated with the various reagents, as described above. The two tubes are then compared with the scale of standards. The method is not applicable to solutions containing adrenaline, which also reduces Wavelet's reagent, even in absence of ammonia. Details are given for applying the method to morphine hydrochloride syrup (Codex Argentin), opium powder, Laudanum Sydenhami, and tincture of opium. T. H. P.

Assay of Ext. Cocae Liq. B.P.C. and Ext. Cocae. W. A. N. Markwell. (*Pharm. J.*, 1935, **134**, 416–417.)—The assay of coca and its preparations may yield different results by different methods, and even if a standard method (such as that in the B.P.C. 1934) is used, different analysts may not obtain the same result. These discrepancies have been found to be due to insufficient extraction with immiscible solvents and also to the presence, or absence, of volatile bases in the final residue. The author suggests that the B.P.C. assay process for Ext. Cocae Liq. should be modified to include repeated extractions of the ammoniacal solution by successive portions of ether until the extraction is complete, and that the extraction of this ethereal solution with dilute acid should be repeated until the extraction is complete, the solution being tested in each case with Mayer's reagent. It is also suggested that the final ethereal solution be washed with a little water to remove traces of ammonium salts, as recommended by Self (*Pharm. J.*, 1915, **40**, 585; Abst., ANALYST, 1915, **40**, 329), and that the final residue be dehydrated with absolute alcohol. In addition, the volatile bases should be excluded by heating the alkaloidal residue at 80° C. for 2 hours before titration. Since the physiological action of coca is essentially that of cocaine, the author considers that the assay of this drug should be based on the content of non-volatile alkaloids calculated as cocaine, rather than upon the total alkaloids, including the volatile bases. S. G. S.

New Method for the Determination of Pilocarpine and its Salts. J. A. Sanchez. (*Ann. Chim. anal.*, 1935, **17**, 122–123.)—The method is based upon the fact that, when pilocarpine is heated with sodium or potassium hydroxide, the internal ester, of which it consists, is decomposed and a salt of pilocarpic acid is formed. This acid is monobasic and can be titrated with phenolphthalein as an indicator. For the determination of the free base, a quantity of not less than 0·05 g. is dissolved in 10 ml. of a mixture of two volumes of 95–96 per cent. alcohol and one volume of water in a flask with a long neck. To this is added 10 ml. of *N*/10 sodium hydroxide solution and 111 drops of 2 per cent. phenolphthalein solution, the mixture being heated in a boiling water-bath for 5 minutes. After the flask and its contents are cooled, 5 ml. of 95 per cent. alcohol are added and the whole titrated with *N*/10 sulphuric acid. The number of ml. of acid used, subtracted from 10 and multiplied by 0·0208, gives the amount, in grams, of the pilocarpine present. For the determination of the salts of pilocarpine, a solution containing 0·5 g. per 100 ml. of the hydrochloride or nitrate is prepared with the alcohol-water mixture described above. Into a small flask having a long neck, 10 ml. of this solution is placed, followed by 111 drops of the phenolphthalein solution. *N*/10 sodium hydroxide solution is then added until a pale rose colour is obtained. At this stage the hydrochloric or nitric acid is present as the sodium salt, and the pilocarpine, which does not affect the indicator, is liberated. To this mixture, 10 ml. of *N*/10 sodium hydroxide solution are added, the flask is heated in a boiling water-bath for 5 minutes, then cooled, 5 ml. of alcohol added as before and the solution titrated with *N*/10 sulphuric acid. The factor for the hydrochloride is 0·02445, and for the nitrate 0·0271. S. G. S.

Assay of Papain. A. K. Balls, T. L. Swenson and L. S. Stuart. (*J. Assoc. Off. Agr. Chem.*, 1935, **18**, 140–146.)—The method advocated depends upon the titration, in alcohol, of casein which has been digested at its *iso*-electric point by the papain. Thirty g. of a suitable casein are rubbed with a little water in a large mortar, 30 ml. of *N* sodium hydroxide solution are then added, and finally water to a total volume of 1 l. The casein solution must not be heated, and is kept in an ice-box under toluene. In making the determination 10 ml. of the casein solution are placed in a 125-ml. glass-stoppered bottle together with a number of small glass beads, and the bottle is placed in a thermostat at 40° C. After the lapse of sufficient time for the temperature of the bottle and its contents to reach 40° C., 4 ml. of a buffer solution consisting of 280 ml. of 0·2 *M* disodium citrate solution and 850 ml. of 0·1 *N* hydrochloric acid, are added at 40° C. These are followed at once by the enzyme solution, whose volume should not exceed 3 ml. The bottle is shaken vigorously for 10 to 20 seconds, replaced in the thermostat, and incubated for 20 minutes. At the end of this time the contents of the flask are titrated with 0·1 *N* alcoholic potash solution. To the solution in the bottle 1 ml. of a 1 per cent. solution of thymolphthalein in alcohol is added, and then just enough alkali to turn the mixture a distinct blue. The alkali must be added slowly, with shaking, until the blue colour is permanent, and the shaking is continued until all the solid matter has dissolved. The contents of the bottle are then transferred to a 500 ml.-flask, and the bottle is washed out two or three times with a total volume of 25 ml. of 95 per cent. alcohol. To this mixture are added 175 ml. of boiling 95 per cent. alcohol, which causes the colour to disappear, and the titration is continued carefully until the blue colour is restored; this is best seen in daylight. A blank determination is also made in exactly the same manner, except that the solution in the bottle is titrated immediately after the addition of the enzyme solution and not incubated for the 20 minutes. If a series of determinations is made with different amounts of papain, it is possible to plot a graph, with the amount of papain used on the one axis and the amount of 0·1 *N* alkali required in the titration on the other. It is suggested that the amount of papain which is found to be equivalent to 1·0 ml. of 0·1 *N* alkali should be taken as the unit of papain (proteinase activity). S. G. S.

Biochemical

Animal Experiments on the Influence of "Improvers" in Flour. J. von Darányi and St. von Vitéz. (*Z. Unters. Lebensm.*, 1934, 68, 597–612.)—Experimental feeding trials with controls were made upon rats, mice and dogs, using flour to which different "improvers" were added. The proportions used were 0·1 g. of sodium perborate, 3 g. of ammonium persulphate, and 1 g. of benzoyl peroxide, respectively, to 5 kg. of the flour in the form of a porridge and as bread. The results showed measurable retardation of growth and symptoms of disease. There was a marked falling-off in body weight, and the symptoms of poisoning included excoriation and proliferation of the nose together with much depilation. Ammonium persulphate was not so actively injurious as were sodium perborate and benzoyl peroxide, these producing effects similar in nature and extent.

Micro-Determination of Chloride in Tissues. K. Linderstrøm-Lang, A. H. Palmer and H. Holter. (*Compt. rend. Lab. Carlsberg*, 1935, 21, 1–5.)—The tissue to be analysed (which should contain between 4 × 10^{-4} and 20 × 10^{-4} mg. of chlorine, is placed in a reaction vessel of Jena glass, into the bottom of which has been pipetted 0·07 ml. of a solution containing 1·2 g. of sodium nitrate and 0·4 g. of disodium hydrogen phosphate ($Na_2HPO_4,12H_2O$) in 14 ml. The water is evaporated in a drying oven at 106° C., and the incineration is then carried out by cautious heating with a Bunsen burner. If possible, preliminary heating at 300° C. for 10 minutes in a muffle-furnace should be employed. During the heating in the Bunsen flame the temperature should be kept as low as possible, and the incineration is stopped when the brown coating of tar, which forms inside the vessel, has disappeared. After incineration, 0·5 ml. of 0·17 *N* nitric acid solution is added. This solution is then titrated electrometrically with 0·02 *N* silver nitrate solution containing per 100 ml. 1·2 g. of caustic soda, 0·4 g. of disodium hydrogen phosphate and 3·4 ml. of 5 *N* nitric acid. The reaction-vessel is used as one half of the cell, and a silver wire dipping into the solution acts as an electrode. The other half of the cell is the jet of a micro-burette which has a side-tube fused into it, and this contains another silver wire fixed into position with a suitable cement. Both wires should be cleaned in cold dilute nitric acid. The electrodes are connected with an Otto-Wolff potentiometer, set so that the galvanometer gives no deflection when the potential difference is 210 millivolts, corresponding with a silver concentration in the titration cell of $0{\cdot}05 \times 10^{-4}$. This concentration would be produced by adding 0·00013 ml. of 0·02 *N* silver nitrate solution to the 0·5 ml. in the titration cell. The titration is carried out by a series of short immersions of the tip of the burette in the liquid being titrated (*cf.* Linderstrøm-Lang and Holter, *Compt. rend. Lab. Carlsberg*, 1934, **20**, No. 11), the duration of immersion varying according to the stage of the titration and the excess pressure in the burette. The key connecting the galvanometer is kept closed the whole time, and the deflection is observed every time the tip of the burette is immersed (*i.e.* every time the circuit of the cell is closed). The point at which the deflection changes its direction (corresponding with a potential of 210 millivolts in the cell) can be determined with an accuracy of 0·0002 ml. of silver nitrate solution, if care is taken to keep the excess pressure in the burette very small near the end-point of the titration. S. G. S.

Analysis of Albumin and Globulin in Biological Fluids by the Quantitative Precipitin Method. E. Goettsch and F. E. Kendall. (*J. Biol. Chem.*, 1935, **109**, 221–231.)—This method involves (i) the preparation of antisera that will precipitate all the antigenic components of one fraction without marked cross-precipitation of other fractions; (ii) the standardisation of these antisera with known quantities of serum albumin and serum globulin; (iii) the determination of albumin and globulin in unknown biological fluids by comparison with the standardisation curves of the antisera. Albumin and globulin fractions are prepared from normal dog serum. The globulin is precipitated at half-saturation with ammonium sulphate, washed, dissolved in saline and re-precipitated twice to remove traces of albumin. The filtrate from the original precipitation of the globulin is used for the albumin fraction. Both preparations are dialysed free from ammonium sulphate and analysed for total and non-protein nitrogen by a modified Pregl micro-Kjeldahl method (Weech, Snelling and Goettsch, *J. Clin. Inv.*, 1933, **12**, 193). The alum-precipitated suspensions of the albumin and globulin fractions are prepared and injected into the ear veins of rabbits. About 11·4 mg. of antigen is given per rabbit in a course of eighteen injections. Rabbits showing a sufficiently high antibody titre in test bleedings are bled from the heart and the antisera to each antigen are pooled. Both antisera are sterilised by filtering through a Berkfeld candle; merthiolate* is added to a concentration of 0·01 per cent., and the sera are stored in small rubber-stoppered bottles in an ice box. A serum of known albumin- and globulin-content is used for standardisation. This should be diluted with sterile saline so that concentrations of 0·1 to 0·4 mg. of albumin and 0·1 to 0·4 mg. of globulin per ml. are available. Duplicate samples of the diluted antigens are measured out into sterile Wassermann tubes, the volume is made up to 2 ml. with saline and 1 ml. of the homologous antiserum is added to each tube. Blanks should be set up with 2 ml. of saline and 1 ml. of antiserum. The contents of each tube are thoroughly mixed by carefully stroking the tube inside and giving it a swirling motion. The tubes are plugged with rubber stoppers, kept at 37° C. for 2 hours, and placed in the ice-box overnight. They are then centrifuged for 10 minutes in a small angle-centrifuge which should be placed in a refrigerator kept at 4° C. The supernatant fluid is carefully decanted without loss of the precipitate, and the tube is inverted for a few minutes on a towel to drain. Excess fluid is wiped off, and the tubes are returned to a rack embedded in ice and water. Each precipitate is then dispersed in 2 ml. of ice-cold saline, allowed to stand for 30 minutes in ice-water, centrifuged and carefully drained. After a second washing in 2 ml. of saline in a similar manner, the precipitate is dissolved in 5 drops of *N* sodium hydroxide solution, and rinsed into a micro-Kjeldahl flask, and the nitrogen is determined. The amount of nitrogen precipitated is then plotted against the quantity of antigen used. For biological fluids, the total nitrogen is first determined to estimate the approximate albumin and globulin concentrations. Dilutions of the fluid containing about 0·30 mg. of albumin and 0·25 mg. of globulin are set up in duplicate with the two antisera, using the above technique. The amounts of globulin and albumin in the sample are then determined by reference to the standardisation curves. The serum used for standardisation may have its albumin and globulin content determined by the method of Howe (*J. Biol. Chem.*, 1921, **49**, 109). S. G. S.

Glyoxalase as a Reagent for the Quantitative Micro-estimation of Glutathione. G. E. Woodward. (*J. Biol. Chem.*, 1935, **109**, 1–10.)—Reduced glutathione may be determined in tissues by a manometric method, which depends on the measurement of the activating effect of glutathione on acetone-yeast glyoxalase. The effect of glutathione is specific, neither cysteine, thioneine, ascorbic acid, nor oxidised glutathione producing any activity. Measurements are made in a Barcroft–Warburg manometric apparatus at 25° C., the manometer cups having a single side-bulb of about 0·8 ml. capacity and a total volume of about 18 ml. For a determination the following materials are measured into the main chamber of each manometer cup:—0·5 ml. of glutathione-free acetone-yeast (15 to 20 per cent. suspension) (see also *J. Biol. Chem.*, 1934, **104**, 281), 0·2 ml. of methyl-glyoxal (10 mg. per ml.), 0·4 ml. of sodium carbonate (0·2 *M* solution), and water to make a total volume of 2 ml., including the measurements in the side bulb. By mixing the yeast and methyl-glyoxal first, the observed blank gas evolution caused by a slight reaction between these two is cut down, since the greater part of this reaction occurs before the manometer readings can be started. After tipping, the apparatus is left for 4 minutes, and readings are then taken every 5 minutes over a period of 20 minutes. The amount of carbon dioxide produced in 20 minutes is plotted against the amount of glutathione, and the standard glutathione curve is traced through these points. The glutathione standards are usually 0·025, 0·05, 0·1, and 0·15 mg. of glutathione in solution in the side-bulb. After a standard curve has been made, a portion of the solution to be analysed is added to a similar amount of yeast, and the activating effect is observed. By reference to the standard curve the quantity of glutathione present can be determined. For blood and tissues, a sulphosalicylic acid (2 per cent.) protein-free filtrate is used, and this is neutralised with 0·2 *M* sodium bicarbonate solution, with methyl orange as an indicator. The following concentrations and amounts of solution are recommended:—For whole blood 0·5 ml. of a 1 : 5 filtrate, for red blood cells 0·5 ml. of a 1 : 10 filtrate, for blood plasma 0·5 ml. of a 1 : 1·5 filtrate, and for animal tissues 0·25 ml. of a 1 : 5 filtrate. Glutathione values for tissues are lower by this method than by iodimetric titration, but this discrepancy does not arise in the case of blood. As a rule, the differences between the iodimetric and manometric determinations can be accounted for by 2 : 6-dichlorophenolindophenol titrations. S. G. S.

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* "Merthiolate" is the proprietary name of sodium ethyl-mercurithiosalicylate, $C_2H_5.Hg.S.C_6H_4COONa$.—*Editor.*

Iodimetric Determination of Cysteine. T. F. Lavine. (*J. Biol. Chem.*, 1935, **109**, 141–145.)—In the methods proposed by Lucas and King (*Biochem. J.*, 1932, **26**, 2076) and Virtue and Lewis (*J. Biol. Chem.*, 1934, **104**, 415), cysteine is determined by titrating the iodine liberated from potassium iodide at 0° C. in *N* hydrochloric acid solution. At this temperature the excess of iodine present, as well as the time interval before titration, must be limited to as small a value as possible, owing to the tendency of the oxidation to proceed beyond the disulphide stage. If, however, the concentrations of both the hydrochloric acid and potassium iodide are 1 *M*, the titrations can be carried out at room temperature. Under these conditions the indirect iodimetric determination of cysteine gives results consistent with its oxidation to cystine. S. G. S.

Vitamin C in Indian Foodstuffs. A. R. Ghosh and B. C. Guha. (*J. Indian Chem. Soc.*, 1935, **12**, 30–36.)—The ascorbic acid (vitamin *C*) in the trichloroacetic acid extracts of Indian foodstuffs has been determined by titration with 2:6-dichlorophenolindophenol. In all determinations it was found advisable to add 1 ml. of glacial acetic acid to inhibit the decolorisation of the dye by the trichloroacetic acid. A progressive decrease in the ascorbic acid content was observed for mangos, from one tree, when examined at the bud, unripe and ripe stages. This is the opposite of that known to take place during the germination of the seed. The same phenomenon has been observed with the guava. The guava (up to 1·0 mg. per g.), the mango (*langra* variety) (up to 0·69 mg. per g.), and the lichi (0·48 mg. per g.) are the richest sources of vitamin *C*; but varieties of mango differ markedly in their vitamin-content. Indian orange contains about 0·18 mg. per g., and the lemon about 0·19 mg. per g. Germination increases the ascorbic acid content of *mung* 7·8 times (0·04 to 0·31 mg. per g.), calculated on a dry-weight basis, and it is probable that trichloroacetic acid does not extract all the vitamin *C* from the germinated *mung*. S. G. S.

Bacteriological

Moisture Requirements of Mould Fungi, with special Reference to Mildew in Textiles. L. D. Galloway. (*J. Text. Inst.*, **1935**, **26**, 123T.)—The criterion which determines the growth of mould fungi may be either that the materials themselves are damp, or that the atmosphere in which they are stored is too humid. For "dry" materials the atmospheric humidity is obviously the vital factor. Certain deliquescent substances (*e.g.* glycerin and magnesium chloride) are capable of causing increased "liability" to mildew, but this effect is much less than if all the extra moisture were available for growth, and it is attributed to a stimulant or nutrient action. A considerable variation is found in the moisture requirements of some of the commoner groups of mould fungi, the minimum relative humidity varying from 75 to 95 per cent. The types having a low moisture-requirement include *Aspergillus glaucus*, *A. candidus*, *A. versicolor*, and species of *Penicillium*. These will, therefore, cause trouble under moderate storage conditions. The "safe" figure for the humidity of the storage depends on the organisms that are liable to occur rather than on the nature of the material. S. G. S.

Organic

Chloranil as a Differential Reagent for Amines. J. Sivadjian. (*Bull. Soc. Chim.*, **1935**, **2**, 623–625.)—A method previously devised by the author for testing for certain bases was to heat the hydrochloride of the base with a solution of chloranil in epichlorhydrin (*J. Pharm. Chim.*, **1931**, **13**, 528). It is now found that this reaction affords a generally applicable means of differentiating between primary, secondary and tertiary amines, which give, respectively, red, violet and green colours with chloranil. The reaction occurs with simple aliphatic amines as well as with more complex compounds in which phenyl, hydroxyphenyl or naphthyl groups are substituted in the aliphatic chain. A few exceptions were found. Thus dimethylaminomethylcoumaran gave no characteristic colour, whilst ephedrine, a secondary amine, gave the colour reaction of a tertiary amine. S. G. C.

Wax of the Felted Beech Coccus. B. K. Blount. (*J. Chem. Soc.*, **1935**, 391–393.)—An analysis has been made of the felted mass of wax fibres that the insect *Cryptococcus fagi*, Barensprung, which lives on the trunks and large branches of the beech tree, secretes as a protection. Repeated crystallisation caused little alteration in the m.p. (80·2 to 81·3° C.), and on hydrolysis approximately equal amounts of cerotic acid, m.p. 81·1 to 82·0° C., and ceryl alcohol were separated. Confirmation of their identity was obtained by dissolving the alcohol in acetic acid and oxidising with potassium dichromate. The mixture was cooled and the separated solid collected; since the m.p. was not sharp, the acid was converted into its calcium salt and purified by extraction with hot alcohol and chloroform, and the regenerated acid, when crystallised from acetic acid, melted at 81·5 to 82·3° C., whilst the mixture with an equal amount of the acid prepared by hydrolysis of the wax, had m.p. 81·2 to 82·0° C. By applying the data contained in the paper by Piper, Chibnall and Williams (*Biochem. J.*, 1934, **28**, 2175) to the products isolated from the wax, an idea of the approximate composition was obtained. A mean chain length of 25·6 was indicated by the m.p. of the acetate of the alcoholic component (58·7–59·1° C.); the m.p. of the free alchol (77·5 to 78·0° C.) indicated the mixture of this mean composition to be at least ternary; this m.p. and that of the derived acid are satisfied by a mixture of about 80 per cent. of the C_{26} compound with 20 per cent. of a mixture of C_{24} and C_{28} compounds, the former predominating. The acid component (m.p. 81·1 to 82·0° C.) gave an ethyl ester of m.p. 60·4–60·8° C., and is therefore a ternary mixture containing 70 to 80 per cent. of the C_{26} acid with 30 to 20 per cent. of the C_{24} and C_{28} acids. D. G. H.

Improved Ferricyanide Reagent for the Detection of Oxycellulose. W. F. A. Ermen. (*J. Soc. Dyers and Color.*, 1935, **51**, 127–129.)—The method previously described (Abst., ANALYST, 1928, **53**, 670) has the disadvantage that the undamaged parts of the material are liable to brown staining by ferric hydroxide formed by hydrolysis of the ferric sulphate used. This may be prevented by the presence of acetic acid. The procedure is, therefore, modified as follows:—Two stock solutions are made: (i) 14 per cent. ferric ammonium alum solution, and (ii) 7 per cent. potassium ferricyanide solution. The actual solution used contains 2 ml. of (i), 1 ml. of (ii), 8 ml. of glacial acetic acid, and water to 100 ml. The samples of material to be tested are treated with the cold reagent in test-tubes or small flasks, which are then kept in a boiling water-bath for 5 minutes. After being washed in cold water until all the reagent is removed, the samples are treated with 30 per cent. acetic acid solution and the vessels immersed for 5 minutes in a boiling water-bath. The samples are then washed again and boiled in 10 per cent. ferrous sulphate solution acidified with sulphuric acid, in order to develop the colour. Under such conditions the blue colour produced is proportional in intensity to the degree of the tendering to which the material has been subjected. The reagent responds equally well to oxidised celluloses of various types, whether formed by treatment with hypochlorite, acidified permanganate or dichromate, or even sodium hydroxide and air, but does not react with hydrocellulose. The reaction is not mere reduction of ferric ferricyanide to Prussian blue, but is probably due to absorption by the tendered cotton of some derivative of potassium ferricyanide, which is afterwards changed to Prussian blue by reduction with the ferrous salt used as "developer." T. H. P.

Inorganic

Effect of Nitric Acid Fumes on Certain Elements. E. Montignie. (*Bull. Soc. Chim.*, 1935, **2**, 625–626.)—The element was kept in contact with the vapour of fuming nitric acid for periods up to 2 months at 15 to 18° C. The following products were formed:

Element	Product formed
Chlorine	Chloric acid; no perchloric acid.
Bromine	Bromic acid.
Iodine	Iodic acid.
Sulphur	No action.
Tellurium	No action.
Selenium	Selenium dioxide.
Arsenic Antimony } ..	Protective oxide film.
Phosphorus ..	Mixture of phosphoric and phosphorous acids.

S. G. C.

Argentometric Determination of (*a*) Sodium Sulphide and Sulphydrate; (*b*) Alkali and Sulphide in Sodium Aluminate. (*a*) N. A. Tananaeff and J. N. Kremer. (*Z. anal. Chem.*, 1935, **100**, 271–273.) **(*b*) N. A. Tananaeff and M. A. Schachowa.** (*Id.*, 273–276.)—(*a*) The equation $NaSH + 2AgNO_3 = Ag_2S + NaNO_3 + HNO_3$ shows that, unlike sodium sulphide, the sulphydrate produces free acid when treated with silver nitrate. Two measured portions of the sulphide solution are thoroughly shaken with a known excess of silver nitrate solution. The first portion is then shaken with a small excess of saturated sodium chloride solution, and titrated with standard alkali (methyl orange as indicator). The mixed precipitate settles so quickly that filtration is unnecessary. In the other portion, the excess of silver is ascertained with thiocyanate and ferric alum, no filtration being required. The first titration gives the quantity of sulphydrate, the second the amount of silver precipitated by sulphide and sulphydrate.

(*b*) The aluminate solution to be titrated is diluted with water to 0·1 *N* alkalinity. Two aliquot portions are required. (1) Fifty ml. are pipetted into a graduated 250-ml. flask and made up to the mark with 0·1 *N* silver nitrate solution. The liquid is well mixed by shaking and filtered through a dry paper, the first portions of the filtrate being rejected. Fifty ml. of the clear filtrate are titrated with 0·1 *N* thiocyanate solution (ferric alum indicator). The titration gives the excess of silver over that precipitated by the sodium aluminate ($2NaAlO_2 + 2AgNO_3 + 3H_2O = Ag_2O + 2Al(OH)_3 + 2NaNO_3$), carbonate, and sulphide. (2) Twenty-five ml. are treated in a conical flask with 50 ml. of 0·1 *N* silver solution, 50 ml. of hot water, and 10 ml. of sulphuric acid (1 : 4). The silver oxide dissolves on agitation, leaving silver sulphide. Titration of the excess silver indicates the amount of sodium sulphide. In a third portion the alumina is determined gravimetrically, 50 ml. being run into a concentrated solution of ammonium chloride containing a fivefold excess of the salt; the liquid is diluted to 100 ml. with hot water, thoroughly stirred, and filtered after a short time. The precipitate is washed with ammonium nitrate solution and converted into Al_2O_3 by the usual method.

In a third paper (*id.*, 276–280), Tananaeff and Chalat describe the argentometric determination, along the same lines, of baryta and barium sulphide in barium aluminate.

W. R. S.

New Indicators for Argentometry. E. Chirnoaga. (*Z. anal. Chem.*, 1935, **101**, 31–38.)—(*a*) *Diphenylcarbazone* in 0·2 per cent. alcoholic solution has a red colour. This solution (5 to 8 drops) is added to a neutral halide (10 ml. of 0·1 *M*) solution, with 2 ml. of 0·4 per cent. starch solution. The liquid is titrated with 0·1 *M* silver nitrate solution during thorough agitation. The end-point is shown by the following transitions: from pale-red to violet for chloride, from yellowish to green for bromide and iodide, from pink to blue for thiocyanate. The colour change is reversible for a short time. The error is 0·2 to 0·4 per cent. If acid, the solution is made just alkaline to methyl orange with sodium bicarbonate, and boiled to expel carbon dioxide.

(*b*) *Ferrous ferricyanide.*—Two solutions are freshly prepared: (1) potassium ferricyanide, 2·195 g. per l.; (2) ferrous sulphate, 2·78 g. per l. The indicator is made by pouring 6 ml. of the iron solution into a flask containing 100 ml. of water, and adding 8 ml. of the ferricyanide solution during agitation. The blue solution is stable if kept in the dark. The 0·1 *M* chloride solution (10 ml.) is treated with 1 to 2 ml. of indicator and 3 to 5 drops of *M* sodium acetate solution, and titrated with silver nitrate. The silver chloride remains colloidal and appears blue; at the end-point it rapidly turns white. With bromide and iodide, the colour change is from green to yellow; with thiocyanate, from blue to grey. The colours are more easily observed if the vessel is placed on white paper. Greater accuracy is attained if a second titration is carried out in which the indicator and acetate are not added until all but about 1 ml. of the silver solution has been added. The error is said to be 0·2 to 0·4 per cent.; the titration of bromide, however, is not so sharp, as the precipitate is more sensitive to light. Acid solutions are neutralised as under (*a*), but no acetate solution must be added. Mixed halide solutions can be titrated by the method. W. R. S.

Alkalimetric Determination of Lead in Alloys. N. A. Tananaeff. (*Z. anal. Chem.*, 1935, **100**, 394–396.)—The alloy (0·2 to 0·3 g.) is dissolved by boiling with strong sulphuric acid. When decomposition is complete, the contents of the flask are diluted with 100 ml. of hot water, and digested on the water-bath. After cooling, the precipitate is collected and washed free of acid by water saturated with lead sulphate, and finally with alcohol. Filter and precipitate are transferred to a conical flask, and boiled for 2 minutes with a measured excess of 0·1 *N* sodium carbonate solution. The lead carbonate is filtered off and washed with hot water; the excess alkali in the filtrate is titrated with 0·1 *N* acid and methyl orange. The hydroxides of tin and tervalent antimony do not react with sodium carbonate. The time required for an assay is 1¼ to 1½ hours, and the error varies between —0·7 and +0·28 per cent. W. R. S.

Separation of Mercury from Arsenic, Antimony, and Tin. W. Hiltner and W. Gittel. (*Z. anal. Chem.*, 1935, **101**, 28–31.)—The precipitation of mercuric sulphide by ammonium chloride from a sodium sulphide solution provides a satisfactory separation of mercury from arsenic and antimony, but not from tin; this is partly precipitated, while some mercury remains in solution. The separation is complete if the following process is adopted:—The clear sulphide solution is treated with a strong solution of about 5 g. of sodium tartrate, and

30 per cent. hydrogen peroxide is added, drop by drop, until the precipitation of mercuric sulphide is complete, and then 1 ml. in excess. The solution is boiled until the hydrogen peroxide is decomposed, cooled, treated with 1 g. of sodium oxalate, and again boiled until the evolution of gas has ceased. The mercuric sulphide is collected in a porous glass crucible and washed with weakly alkaline water containing a little tartaric acid. The other metals are converted into arsenate, antimonate, and stannate, whilst mercuric sulphide resists oxidation.

W. R. S.

Determination of Iron in Presence of Titanium. W. M. Thornton and R. Roseman. (*J. Amer. Chem. Soc.*, 1935, 57, 619–621.)—When a solution of ferric and titanic sulphates in dilute sulphuric acid is passed through a Jones reductor, both elements are reduced to the lower sulphates, and it is necessary to re-oxidise the titanium prior to the determination of the ferrous iron with permanganate. It was found that bubbling air through the reduced solution "slightly acidified with sulphuric acid" for 10 to 15 minutes was effective for selectively oxidising the titanium. The results suggest, however, a slight compensating error, and the authors conclude that the matter requires further investigation.

S. G. C.

Determination of Cobalt by means of Nitroso-β-naphthol. L. Philippot. (*Bull. Soc. Chim. belg.*, 1935, 44, 140–153.)—Following precipitation of cobalt by means of nitroso-β-naphthol, it is recommended that, in preference to the usual calcination of the precipitate, it be decomposed, after thorough drying, by heating with fuming nitric acid (sp.gr. 1·5), followed by evaporation with sulphuric acid. The determination is finished by precipitating the cobalt as cobaltic hydroxide, which is dissolved in sulphuric acid and hydrogen peroxide, and the cobalt is finally determined by electro-deposition, according to the usual methods.

S. G. C.

Determination of Small Quantities of Iodide. Application to the Determination of Chromate and Silver. M. L. Jean. (*Bull. Soc. Chim.*, 1935, 2, 605–616.)—Iodide is oxidised by bromine to iodate, which is determined by interaction with iodide, yielding iodine which may be titrated with thiosulphate. Six atoms of iodine are formed for each atom of combined iodine in the original solution. The solution (30 to 50 ml.) containing 0·01 to 0·04 g. of iodine as iodide, is, if necessary, acidified with sulphuric or hydrochloric acid. About 30 ml. of bromine water (containing 10 ml. of bromine and 20 g. of potassium bromide per l.) are added in excess of that just required to colour the solution yellow. After keeping for 10 minutes, the vessel is placed in an ice-bath; 5 ml. of formaldehyde (40 per cent. solution) are added, followed, drop by drop, by sodium hydroxide solution until the yellow colour is discharged. The vessel is removed from the ice-bath, and, after 5 minutes, 5 ml. of glacial acetic acid and 5 ml. of potassium iodide solution (20 per cent.) are added. The liberated iodine is titrated with $N/10$ thiosulphate solution, starch being used as indicator. For quantities of iodine less than 0·01 g., smaller amounts of bromine water and formaldehyde are used, *viz.* 25 ml. and 2 ml. respectively, and $N/50$ or $N/100$ thiosulphate solution is employed for the titration. The purpose of the formaldehyde is to reduce the excess of bromine. The reduction occurs in alkaline solution, but it should be noted that the solution should not be made alkaline before adding formaldehyde, since bromate would tend to be formed. Results in excellent agreement with the theoretical were obtained with 0·0005 to 0·05 g. of potassium iodide. The process is stated to be exact in presence of sulphide, sulphite, thiosulphate and oxalate, but ammonium salts and cyanides interfere.

Determination of small amounts of chromate.—The method depends on (*a*) reduction of chromate with a measured excess of potassium iodide in dilute sulphuric acid solution, (*b*) elimination of the iodine formed, (*c*) determination of the remaining iodide. To the chromate solution (containing less than 0·003 g. of chromium) are added 20 ml. of a standard potassium iodide solution (1·5 g. per l.) and 2 ml. of 1:1 sulphuric acid. The solution is diluted to 100 ml., heated to boiling, and a current of steam is passed into the liquid in order to secure complete removal of iodine. The solution is cooled to room temperature, and the remaining iodide is determined by the method described above. If n and N ml. of $N/50$ thiosulphate solution are required, respectively, in the determination and in the standardisation of the potassium iodide solution added, the weight of chromium present is $(N - n) \times 0{\cdot}05777$ mg. Good results were obtained in test experiments with 0·3 to 2·4 mg. of chromium as dichromate.

Determination of small amounts of silver.—To the silver solution is added an excess of standard potassium iodide solution. After mixing, 10 ml. of barium nitrate solution (5 per cent.) and 10 ml. of sodium carbonate solution (5 per cent.) are added, producing a precipitate of barium carbonate, which functions as a collecting agent for the silver iodide. The liquid is diluted to 100 ml. and filtered, and the unprecipitated iodide present in 50 ml. of the clear filtrate is determined by the process described above. The results with 10 to 70 mg. of silver showed a maximum error of +0·3 mg. S. G. C.

Reactions occurring in the Iodimetric Determination of Chromate. F. L. Hahn. (*J. Amer. Chem. Soc.*, 1935, 57, 614–616.)—Experiments are described which show that when iodide is employed to reduce chromate in slightly acid solution in the presence of sodium thiosulphate, a complex compound is formed between tervalent chromium and thiosulphate, which reacts slowly with iodine. For example, to 200 ml. of water were added 10 ml. of chromate solution (0·1 *N*), 10 ml. of iodide solution (1 *N*), and a quantity of thiosulphate nearly, but not quite, equivalent to the chromate, and the mixture was acidified with 50 ml. of 2 *N* hydrochloric acid. The presence of free iodine could then be verified in the solution by means of starch. The point stressed by the author is that, in spite of the presence of free iodine, thiosulphate can also be detected by, *e.g.* the sodium azide reaction, during a period of several minutes from the time of acidification. It was, therefore, concluded that determination of chromate by adding iodide and thiosulphate, and subsequently titrating back the excess of thiosulphate with standard iodine solution, is inaccurate, unless a long period is allowed for the chromium-thiosulphate compound to react with the iodine. It is pointed out that thiosulphate only forms the complex with *nascent* chromic salt formed during the reaction of chromic acid with iodide, and that thiosulphate does not react with pre-formed chromium salt. Thus it is satisfactory to titrate with thiosulphate the iodine liberated when iodide is added to acidified chromate solution. S. G. C.

Determination of Tellurium in Tellurium-lead. E. Kröner. (*Chem.-Ztg.*, 1935, **59**, 248.)—The following method is proposed for testing the tellurium-content of tellurium-lead containing about 0·05 per cent. of tellurium. A sample of the lead from which the tellurium-lead has been manufactured must be available. A 20-g. sample is dissolved in sufficient 1 : 1 nitric acid. Oxides of nitrogen are removed by boiling, followed by the addition of 5 to 10 ml. of bromine water, the solution being concentrated by boiling until the separation of lead nitrate crystals commences. The liquid, after cooling, is diluted to 500 to 600 ml., and titrated with $N/50$ permanganate solution. A "blank" determination is carried out on a 20-g. sample of the plain lead, and the volume of permanganate solution used, which is usually small, is deducted from that required in the titration of the tellurium-lead. In the titration tellurous acid is oxidised to telluric acid; 1 ml. of $N/50$ permanganate $\equiv$ 0·00102 g. of tellurium. A turbidity of hydrated manganese dioxide is formed, during the titration, in proportion to the amount of tellurium oxidised. This does not interfere with the determination of the smaller amounts of tellurium, but obscures the end-point when more than 0·05 g. of tellurium is present. S. G. C.

Microchemical

Ammonium Molybdate as a Microchemical Reagent. C. van Zijp. (*Pharm. Weekblad*, 1935, **72**, 414–418.)—Except where otherwise stated, the reaction should be carried out by placing a very small crystal of ammonium molybdate in the centre of a drop of a solution containing the sample on a microscope slide; scratching or other aids to crystallisation are unnecessary. Aluminium sulphate gives crystals in squares, rectangles or parallelograms having an angle of 87°, which may overgrow one another to form rosettes, and which show interference colours of the first order. Formation of ammonium alum is avoided by the use of aluminium nitrate or, preferably, of sodium molybdate and aluminium sulphate. The test is not specific, and zinc, nickel, cobalt, chromium, copper, mercury and ferric iron give similar crystals, although metals of the ammonium sulphide group may be removed by adding a slight excess of potassium ferrocyanide solution, the test for aluminium being applied to the solution obtained after removal of the precipitate by filtration. The test is not very sensitive for zinc, and, if manganese is present, a positive result for this metal may be obtained (*vide infra*), and a negative result for the zinc. Nickel or cobalt chloride gives a precipitate which forms crystals slowly, and in testing for cobalt a concentrated solution is desirable. The crystals obtained with copper have rounded angles. The reaction with mercury is very sensitive, but it is an advantage to add the solid salt to a solution of the reagent. Manganese (as chloride or sulphate) slowly deposits, on evaporation, brown-orange prismatic plates, forming pyramids (apex angle 104°, or sometimes when the pyramids are inclined, 54°). Either the sodium or the ammonium salt may be used, and the former produces a cheese-like precipitate which slowly forms short needles. The reaction is unaffected by zinc or aluminium (*vide supra*). Thallium (as nitrate) should be added in the solid form to the reagent, when a dense granular precipitate is formed, and needles subsequently form slowly; the reaction is very sensitive. Silver (as nitrate) gives a cheese-like precipitate containing anisotropic square and octahedral crystals; ferrous sulphate produces a wine-red colour, but no precipitate; strontium or barium (as acetate) produces droplets which show little tendency to crystallise; with cerium, orange or orange-yellow squares, parallelograms or long needles (acute angle 55°) are obtained, but the reaction is not very sensitive. No useful results are obtained with uranium, lead, cadmium, bismuth, lithium, magnesium or calcium.

J. G.

Physical Methods, Apparatus, etc.

Ultra-violet Absorption of Certain Vegetable Oils as an Indication of their Industrial Treatment. J. Guillot. (*Ann. Falsif.*, 1935, **28**, 69–75.)—Curves are given showing the relationship between wave-length (250·0 to 300·0*m*μ) and absorption-coefficient ($e = \log I_0/I$) for 1 per cent. solutions of certain oils in hexane, measurements being made in a cell with quartz walls holding a layer of solution 1 cm. thick (*cf.* Chevallier and others, Abst., ANALYST, 1932, **57**, 789; *Bull. Soc. Chim. Biol.*, 1932, **14**, 1076; 1932, **15**, 358). The mean values of *e* at 270·0*m*μ (for the 1932 and 1933 harvests) were: virgin olive oils, 0·160; refined oils, 0·700; oils from refined pulps, 1·450. These values may be used as a means of classification, subject to allowance for certain points of difference between oils from various localities (*e.g.* "extra" Spanish oils gave values of 0·100 and 0·130; Grecian and Provençal oils, 0·150 to 0·170; Tunisian, Algerian and Moroccan, 0·140 to 0·190). Iodine values of 85 to 86 and 82 to 83 corresponded with values of *e* of 0·180 to 0·190 and 0·150 to 0·160, respectively. The effect of heating in air for 5 minutes is to raise *e* (at 270·0*m*μ) by an amount which increases with a rise in the temperature (150 to 300° C.); arachis oil gave similar results. Neutralisation of arachis oil lowers *e*, owing to elimination of selective absorption due to the fatty acids, unless it is carried out at a high temperature, when the fall is counteracted by the heat effect (*supra*). Treatment in a vacuum produces a sharp rise in *e* between 280·0*m*μ and the shorter wave-lengths, and deodorisation results in a marked increase in *e* at 270·0*m*μ to twice its value; this increase is related to the temperature used. The curves for mixtures of different grades of olive oil suggest that if a sample has a value of *e* over 0·200 it is either refined or contains a quantity of refined oils which is proportional to the excess in the value.

J. G.

Fluorescence of Olive Oils. Influence of Pigments. J. Guillot. (*Ann. Falsif.*, 1935, **28**, 75–78.)—An objection to the fluorescence test for olive oils is that, since the blue fluorescence characteristic of the refined oils disappears when a pigment such as carotene or chlorophyll is added, it is not possible to say whether an oil which does not show the blue fluorescence is a virgin oil or a recoloured refined oil. The author has therefore examined the spectra of the fluorescence produced by light from a mercury arc. Virgin oils irradiated on the surface produced an intense blue-violet band at 380·0 to 460·0$m\mu$, a less intense yellow-green band at 510·0 to 590·0$m\mu$, and an intense red band at 640·0 to 660·0$m\mu$. The spectrum obtained when a layer of oil 1 cm. below the surface was irradiated was less intense throughout, but the blue band was relatively less intense and less uniform, and the others were relatively more intense. If the same oil is decolorised, or if a refined oil is examined, the blue-violet band is very sharp, the yellow band is intensified and the red band is absent. Similar results are obtained both on and below the surface, allowance being made for the decrease in general intensity in the latter case. The results are explained by the supposition that virgin or refined oils contain (i) a substance having a blue fluorescence, and (ii) pigments (which are present originally in virgin oils, and are added in refined and recoloured oils); recoloured oils give rise to a fluorescence having red and orange bands which superimposes itself on that of the oil. The modifications produced in the spectra obtained from the layer below the surface of virgin oil are due to absorption by pigments (chlorophyll, xanthophyll, carotene, etc.) and all these effects may vary with the age of the oil. It is concluded that if the test is applied without taking into account the above considerations, conclusive results can only be obtained when a blue colour is observed (*cf.* T. T. Cocking and S. K. Crews, ANALYST, 1934, **60**, 125). J. G.

Ultra-violet Fluorescence as a Test for Citrus Oils. Determination of Substances Producing the Fluorescence. H. Nicol. (*Perfumery and Ess. Oil Record*, 1935, **26**, 85–87.)—A paper by E. Bottini (*Ann. della Sperim. Agrar.*, 1934, **15**, 61; see also G. T. Dragone, *R. Accad. Lincei*, 1928, Ser. VI, Rend. **8**, p. 604) is summarised critically. The following fluorescence colours are recorded for a single sample of each of the following essential oils in the pure state, and as 0·0034 per cent. solutions in absolute alcohol, respectively:—Mandarin, purple, violet-blue; sweet orange, mustard yellow, dark violet; bergamot, greenish-yellow with purple halo, dark violet; lemon, deeper greenish-yellow with deeper purple halo, dark violet. The corresponding min. concentrations at which fluorescence was visible were 0·0000106, 0·0000212, 0·00021 and 0·00037 per cent. The above-mentioned colours were obtained with drops on a porcelain tile, but they were slightly different when filter-paper was used, the haloes being wider for orange and mandarin oils. Moreover, after distillation of the former the residue had the typical yellow fluorescence, whilst the distillate was blue, and extraction of lemon, bergamot and orange oils with animal charcoal changed the fluorescence from yellow to blue. It is therefore concluded that more than one fluorescent substance is present. Extraction with hide powder did not remove the fluorescence, and tannin is therefore not responsible for it. Of the solid or semi-solid substances which, according to the literature, are known to be present in these oils, methyl methylanthranilate (from mandarin oil), methyl anthranilate (sweet orange oil), bergaptene (bergamot oil) and citroptene (4 : 6-dimethyloxycoumarin, from lemon oil) had a blue fluorescence when dissolved in alcohol, and their general behaviour (*e.g.* on filter-paper) suggested that they are primarily responsible for the blue fluorescence of the oils, the yellow component being due to pigments derived from the cortical glands. If a mandarin or a blood orange is painted with methyl methylanthranilate and methyl anthranilate, respectively, then the characteristic appearance of a blow develops in a few days. It is concluded that a blow ruptures the oil cells, after which the oil spreads on the surface and evaporates, leaving the slightly toxic and less volatile anthranilates; fresh fruits are richer in oil and more tender, and are therefore more susceptible. J. G.

Microscopical Examination of Leather. Optical Properties of Tanned Fibres. I. Refractive Index of Vegetable-tanned Leather Fibres. R. H. Marriott. (*J. Int. Soc. Leather Trades' Chem.*, 1935, **19**, 133–140.)—The refractive index (n) is determined by mounting the fibres in a liquid of known refractive index and observing it under a microscope set for critical illumination, oblique illumination being obtained by means of a disc of cardboard, from which a sector has been cut out, inserted in the condenser mount. The stop is so arranged that the light strikes the side of a fibre, the iris being then closed until all glare vanishes. If the refractive index of the fibre is higher than that of the mounting medium, the brighter edge will be on the same side as the opening in the cardboard-stop, and *vice versa*; coloured fringes on the fibre indicate a close similarity between the refractive indices of the fibre and mountant. Mounting liquids of various refractive indices are obtainable by mixing suitable volumes (V_1 and V_2, respectively) of iodobenzene (n_1, 1·621) and nitrobenzene (n_2, 1·552), and the value is calc. from the expression $(V_1n_1 + V_2n_2)/(V_1 + V_2)$. Investigations with 38 sole leathers indicate that tannin is held in 3 ways, *viz.* (i) as fixed or combined tannin, which is not removed by washing with water and which has only a slight effect on n; (ii) as water-soluble material which is intimately associated with the fibre, and which affects the refractive index; (iii) as water-soluble matter which does not influence n, but which coats the fibres and is scattered throughout the structure of tanned leather without penetrating the micellar structure of the fibres. Although the variations in n for fibres tanned in different ways are insufficient to be used as a means of estimating quality or chemical composition, good leathers have a lower n than poor leathers, the border-line being in the neighbourhood of 1·53. Canada balsam is therefore a very suitable mounting medium, and the mounted fibres of good and poor leathers show a thick and thin outline, respectively.

J. G.

Reviews

SHELLAC. By E. J. PARRY, B.Sc., F.I.C. Pp. 240. London: Sir Isaac Pitman & Sons, Ltd. 1935. Price 12s. 6d.

There are various reasons which combine to make this book one of peculiar interest. To treat of shellac, its production, manufacture, chemistry, analysis, commerce and uses requires a wide knowledge of technical processes, of botany, entomology, chemistry and law. Dr. Parry wrote his first paper on shellac in 1901, and, as we all know, has been intimately associated with this subject ever since, so that when we come to read "Parry on Shellac" it is with great expectations. Sir Harry Lindsay contributes a Foreword to the volume, and remarks that it shows a wonderful grasp of the many complex problems underlying the shellac industry, and that it offers important suggestions. These facts suffice to show that it is a volume which all who have occasion to handle shellac—chemists or others—will wish to acquire.

The first four chapters deal with the origin, production and manufacture of shellac. These give a clear account of the history of the industry and of the insect on whose activities it depends. *Laccifer lacca* is a curious insect; it appears to exist to supply us with lac with which to make our gramophone records, to insulate electrical machinery, and to make profits for merchants. It has a strange life history, and its enemies, parasites—predatory and indirect—are numerous. The industry has been changed from haphazard collection to a semi-scientific one based on study of the various kinds of trees which are the host of *L. lacca* and of the insect and its product. Dr. Parry tells us in a very interesting way how all this has been done and how the crude lac which *L. lacca* lives to produce and then dies in, is subsequently treated to yield the seed lac, button lac, T.N. garnet lac and other varieties known in the world's markets.

Perhaps of even more importance to the analyst are the two chapters following, on the analysis and the chemistry of shellac. The author has very definite views of his own, and not all will agree on some points, but, as there is no right of reply to a review, we will not enter into these. It may, perhaps, be doubted whether Dr. Parry is quite right when he says that the Hübl method for iodine value is the standard in England, in view of the fact that the W.D. specification (quoted in the volume) cites the Wijs method, and that this method is much used by some analysts. Also, it is only fair to Shaefer's work on "Shellac" to point out that the tables facing p. 147 have been incorrectly added, so that the criticism made of them is invalid. The author's long experience of the subject makes his general critical survey ot the chemistry of shellac valuable and lends weight to his criticisms of some of the structural formulae which have been put forward on insufficient experimental basis. The discussion of the fascinating question of how the same lac is formed by the insect from the sap of different kinds of tree is all too brief.

The last chapter is of particular interest, and one which few could have written; it is on the commerce of lac, and gives an intimate account of the way in which this rather specialised trade is carried on; also the types and forms of contract for the various grades of shellac are cited and annotated. An appendix reproduces some original papers and gives a glossary of native terms and a bibliography.

No other volume deals so fully with all aspects of shellac, so that this one is most welcome. It may be hoped, too, that it will stimulate research into the chemistry of the subject, so that the constitution of lac and its relation to the sap of the trees may be really determined; it has not yet been done.

H. E. Cox

CARBON COMPOUNDS: A SCHEME FOR THE DETECTION OF THE MORE COMMON CLASSES. F. E. WESTON. Sixth Edition. Pp. x + 113. London: Longmans, Green & Co. 1934. Price 4s. 6d.

The sixth edition of this very valuable little book has been revised by Dr. F. R. Weston, and its usefulness is greatly increased by the addition of an index, the absence of which has exasperated users of previous issues.

The book opens with a very full discussion of the detection of the characteristic elements, and what follows enables the student to assign most common organic compounds to their particular class; in many instances complete identification is possible without outside reference. In all cases, however, by following the scheme sufficient data are obtainable to enable any intelligent student to proceed to the final stage.

Although the book is very sound and by no means out of date, it would, perhaps, have been advantageous to introduce the characteristics of such commercially important compounds as dibutyl phthalate, triphenyl phosphate, methylethyl ketone, cyclohexanone and tetraline. The use of 2:4-dinitrophenylhydrazine and *p*-nitrobenzoyl chloride might also have been included.

As a result of many years of actual use, the reviewer can safely recommend Weston's "Carbon Compounds" as a thoroughly satisfactory book to place in the hands of those starting a course of qualitative organic chemistry.

HAROLD TOMS

LAC AND INDIAN LAC RESEARCH INSTITUTE. By DOROTHY NORRIS, M.Sc., F.I.C., P. M. GLOVER, B.Sc., and R. W. ALDIS, Ph.D., F.I.C. Pp. vii+53. Indian Lac Research Institute, Nankam. 1934. Price Rs.2.8.

This brochure of 53 pages is published by the Indian Lac Research Institute, and is, in the main, devoted to an account of the work achieved and being done by the Institute. In a dozen pages a brief survey on the various aspects of the lac industry are given, but, as might be expected, no attempt is made to go into any great detail. The actual work of the Institute is described under the headings of Biochemical Research, Chemical and Physico-chemical Research, Entomological Research, and General Activities. Although there is little touching the chemistry or analysis of shellac, this brochure is one which no one interested in the scientific outlook of the shellac industry can afford to be without.

E. J. PARRY

THE NATURAL LOGARITHM. By SIR CHARLES VERNON BOYS, A.R.S.M., LL.D., F.R.S. Pp. 31. London: Wightman & Co., Ltd. Price 2s.

The theory of logarithms, particularly the natural logarithm, is probably accepted by the majority of students without question, and the logarithm is subsequently employed as a mathematical convenience without much thought as to its meaning and origin. This book will give its readers a new outlook and extended appreciation of the derivation of logarithms.

The exposition of the thesis has a geometrical basis and it needs only the most elementary knowledge of the subject to follow the reasoning. A concrete significance is thereby given to the natural logarithm, although the translation of the geometrical relationships to finite numbers requires, as unfortunately all such calculations must, the use of approximations.

The reading of this book will give a new interest and significance to a chapter of mathematics which has sometimes been regarded as closed.

P. BILHAM

JULY, 1935 Vol. 60, No. 712

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Death

WITH great regret we record the death of Percy Arthur William Self, who joined the Society in 1929.

Obituary

CHARLES FREDERICK CROSS

CHARLES FREDERICK CROSS was born in 1855 and died on April 15th, 1935. His father, Charles J. Cross, J.P., of Brentford, Middlesex, was a director of the firm of T. B. Rowe, the well-known soapmakers of that town, so that at an early age, probably, he began to appreciate the relation between chemistry and industry. After four years at King's College, London, where he took prizes for chemistry, geology and German, he embarked, at the age of 18, on a chemical career, with a post as chemist in a sewage works at Barking.

Following similar experience in the Midlands, he spent the year 1876 in Zurich, studying organic chemistry at the University and the Polytechnikum, and then entered Owen's College, Manchester, from which he graduated B.Sc., London, in 1878. He took an active part in the life of the College, speaking at the Union and contributing, for example (1st March, 1878), a paper to the College chemical society on the "Life and Work of Liebig," Dr. (afterwards Sir Henry) Roscoe being in the chair. A piece of research on "The Hygroscopic Properties of Bodies," published in 1879, filled a post-graduate year. He was obviously looking for a line along which to specialise, and the opportunity came in that year. The Barrow Flax and Jute Company, of Barrow-in-Furness, asked Dr. Roscoe to send them a young chemist to investigate difficulties connected with bleaching. He selected Cross, who at once realised that in the chemistry of vegetable tissues there must be a vast unknown field with endless possibilities. His work on the action of bleach on jute, ever afterwards his favourite lignocellulose, led him to the discovery of the chlorination process for the isolation and estimation of cellulose in lignified tissues. He left Barrow in 1881 to continue his researches at the Jodrell Laboratory, Kew, where he worked in association with his college friend, E. J. Bevan, who was interested in cellulose, also from the paper chemist's point of view. Communications dealing with cellulose and coal, jute and lignification appeared under their names in the chemical journals of 1882–3. The result was the partnership of Cross and Bevan, set up in 1885, with laboratories at 3, New Court, Lincoln's Inn—still the home of the firm. The first letter signed "Cross and Bevan" is dated December 15th, 1884; it relates to the supply of sulphite of soda to Philadelphia and foreshadows subsequent world-wide interests of the writers. Bevan had a connection with the paper industry, and their research work led them to play an active part in the development of the bisulphite pulp process of which Mr. George Fry, Mr. C. D. Ekman and Mr. D'Oyley Mears, of Ilford, were pioneers. Cross and Bevan's *Textbook of Papermaking* appeared in 1887. Cross also established himself as an authority on vegetable fibres, and the *Reports on Fibres*, 1886–7 (Colonial and Indian Exhibition), include his now well-known scheme for the analysis of fibres, including α- and β-hydrolysis, chlorination, nitration, and furfural-estimation. Devoted to research, Cross spent as much time as possible at the bench, and the preparation of acetyl and benzoyl celluloses (1889, 1890) was a prelude to the great achievement of his career, the discovery of cellulose sodium xanthate (viscose), which was worked out and patented under the joint names of Cross, Bevan and Beadle in 1892. Cross at once recognised the importance of this derivative of cellulose, soluble in dilute alkaline solutions and capable of reversion to the hydrated cellulose form. The autumn of 1892 was a period of great activity. Clayton Beadle was making viscose, as Cross began to call it, at St. Mary Cray, and discovered the important factor of the age of the soda cellulose. Cross arranged for the development of the product in Germany and in America, and even made enquiries for a machine for producing viscose films. His efforts at first were mainly directed towards the use of viscose as a "filler" for cloth, whereby "effect" surfaces and waterproof and other finishes could be produced. In 1898, however, C. H. Stearn, of Kew, consulted him about the making of electric-lamp filaments from viscose. It was soon found that viscose could be spun at a reasonable speed, and with the invention of the centrifugal spinning box by Topham in 1900 the production of viscose silk on a commercial scale became possible. The Viscose Spinning Syndicate, of which Cross was chairman, gradually brought the process to large-scale production, and its development was undertaken by the Société française de la Viscose in France and by Courtaulds, Ltd., in England (1904), Cross remaining in continuous contact on the research and technical side.

During the next twenty years Cross and his firm became identified with every activity in the cellulose world. By writing, lecturing and the steady output of original work he did everything possible to develop the chemistry and further applications of cellulose.

He was awarded the medal of the Society of Chemical Industry (1916) for "conspicuous services to chemical industry," and was elected a Fellow of the Royal Society (1917). The medal awarded by the Worshipful Company of Dyers was given to him (1919) for a contribution on "Colloidal Tannin Compounds," and he was elected President of the Society of Dyers and Colourists for 1920 and

1921. Always interested in the work of the Royal Society of Arts, he gave the Cantor Lectures in 1920, on "Recent Researches in the Cellulose Industry."

Besides the book on papermaking, he published, with Bevan and others, *Wood Pulp and its Applications* (1911) and the classical *Cellulose, an Outline of the Structural Elements of Plants* (1895). This work was written at Dieppe during a three weeks' summer holiday. To those who knew him the book is Cross himself, speaking, writing, thinking; full of enthusiasm, his ideas pouring out tumultuously, but everywhere giving inspiration for future work.

Cross had a kindly dry humour and was always intensely alive. In his younger days his chief recreation was rowing. He was also very fond of music, playing excellently on the organ and the piano. During the last few years he lived in retirement at Hove, and, unable to walk very much, he owed everything to the devoted care of his wife, who survives him. He married in 1890, and leaves two sons and a daughter.

C. DORÉE

The Determination of Total Alkaloids in Cocoa and of Cocoa-matter in Flour Confectionery.

BY D. D. MOIR, M.SC., F.I.C., AND E. HINKS, B.SC., F.I.C.

(*Read at the Meeting, May* 1, 1935)

PART I

THE DETERMINATION OF TOTAL ALKALOIDS* IN COCOA

THE proposal of another method for the determination of total alkaloids is made, not so much because of any defect in the well-known method of Kunze,[1] but in order that the method may be used for cocoa in the presence of other materials, in particular when the proportion of cocoa is small.

Although this determination remained a difficult problem for many years, it was solved satisfactorily by Kunze in 1894. Later investigators concentrated on the determination of theobromine alone, and a method for the determination of this alkaloid was published by Wadsworth[2] in 1921. Neither of these methods, however, can be applied to mixtures of cocoa with such other materials as are contemplated in this paper.

A full review of the subject is given in the papers of Kunze and of Wadsworth (*loc. cit.*). To determine total alkaloids—theobromine and caffeine, Kunze digests the cocoa with 5 per cent. sulphuric acid, precipitates the alkaloids and protein-like substances with phosphomolybdic acid, regenerates the alkaloids with barium hydroxide, and separates them by solution in hot chloroform. A very pure extract is obtained in this way, although the method has been stated by some to give low results.

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* For convenience, in this paper theobromine and caffeine are referred to as alkaloids.

For theobromine, Wadsworth makes use of the striking solubility of this alkaloid in tetrachloroethane. After a short digestion of the cocoa with water and magnesium oxide, the mixture is boiled directly with the solvent. The greater part of the latter is then removed, and the theobromine is finally precipitated with ether.

The extraction of theobromine from cocoa is rendered difficult by the very low solubility of the alkaloid in water and in most organic solvents, including alcohol. We have, therefore, worked on relatively small quantities of material, even when larger amounts were available. By this means extraction is rendered less difficult, and the requisite volume of the extractant at successive stages can be kept relatively low.

THE METHOD IN OUTLINE.—The cocoa or chocolate is digested repeatedly with 80 per cent. (by vol.) alcohol and a little magnesium oxide and filtered. The filtrate is evaporated, and water is added to replace the alcohol lost. The resulting fluid is clarified with zinc ferrocyanide and filtered, and the filtrate evaporated to very low bulk and extracted with chloroform. Nitrogen is determined in the extract, and the total alkaloids are calculated by use of an appropriate factor.

THE DIGESTION WITH ALCOHOL AND MAGNESIA.—The use of alcohol, although an advantage, is not absolutely necessary in the case of plain cocoa or chocolate, since the same result is obtained by water extraction. It was introduced into this method in view of its application to flour confectionery. Very strong alcohol does not extract the whole of the alkaloids. The magnesium oxide serves two purposes: the removal of interfering substances, colouring matter, etc., which would otherwise be extracted, and the liberation of the alkaloids from the tannate, which some investigators have stated to be present in the roasted cocoa-nib. The removal of the alcohol by evaporation and its gradual replacement by water is accompanied by a separation of fat, loss of alkaloid by reason of its solubility in cocoa butter being prevented by the relatively large bulk of hot water.

THE CLARIFICATION.—Many experiments were carried out before a satisfactory procedure was found. Attempts were made to remove the fat by means of petroleum spirit, evaporating the water phase, and extracting with chloroform. Although fair success was obtained with prepared cocoa or plain chocolate, the method broke down completely when applied to complex foodstuffs, such as cake. Persistent emulsions were encountered at every stage. Furthermore, although theobromine is insoluble in petroleum spirit, caffeine is slightly soluble, and there is thus a risk of some alkaloid being removed with the fat. Search was therefore made for a substance which would precipitate emulsifying substances and fat without removing any of the alkaloids. Lead acetate and sodium hydroxide or ammonia, lead acetate and acetic acid and alumina cream either lead to loss of alkaloid or are not effective in precipitating interfering substances. The success of zinc ferrocyanide as a clarifying agent in other circumstances suggested a possible alternative. It was found that theobromine could be recovered quantitatively from its aqueous solution after the addition of zinc acetate and potassium ferrocyanide. Again, in the case of a chocolate, where emulsifying substances other than fat did not seriously interfere with the chloroform extraction, the same result was obtained for the total alkaloids whether zinc ferrocyanide clarification was used or whether the fat, etc., was simply filtered off. The filtrate obtained after clarification has always, in our experience, been bright and clear whatever material was being dealt with. The volume of precipitate correction for cocoa or chocolate is usually small, and may generally be neglected, but it could be allowed for by determining the fat in a portion of the alcohol extract.

THE FINAL EXTRACTION.—Chloroform was preferred to the hot tetrachloroethane used by Wadsworth for the determination of theobromine alone.

The solubility of theobromine in either water or chloroform at 15·5° C. is only 0·06 g. per 100 ml.[3] Prolonged and vigorous shaking with a large volume of chloroform is absolutely essential to ensure complete extraction of even very small quantities of alkaloid. For quantities of the order of 20 to 30 mg. of alkaloid in 10 to 20 ml. of solution we have found two series of extractions, each consisting of five vigorous shakings with 30-ml. quantities of chloroform, to be sufficient to remove all the alkaloid. The first series usually removes about 90 per cent. of the total.

Although theobromine may be extracted from slightly alkaline or neutral solutions, we have found it preferable to use faintly acid solutions.

TREATMENT OF THE RESIDUE.—The residue, after removal of the chloroform, is clean and almost white, and a good approximation to the alkaloid-content can be obtained by direct weighing. There is, however, present a small quantity of yellowish non-crystalline substance other than the alkaloids of cocoa. For accurate results the nitrogen-content of the chloroform extract must be determined.

Wadsworth has stated that the nitrogen of theobromine cannot be quantitatively determined by means of the Kjeldahl process, owing to partial volatilisation of the alkaloid before decomposition. Jensen[4] believes that a very prolonged digestion is necessary, and that complete conversion of the alkaloidal nitrogen into ammonia is obtained by heating the digestion mixture for at least nine hours after it has become colourless. In a series of experiments, carried out mainly on small quantities of theobromine, we have failed in every case to obtain complete conversion into ammonia. Heating has been continued for long and short periods at high and low temperatures and with several different catalysts, but the results were always low.

We have found, however, that if a little organic matter, such as sucrose, is added before digestion with sulphuric acid, using selenium as catalyst, the alkaloidal nitrogen is converted into ammonia without loss.

Analysis of a chocolate which gave 1·12 per cent. of total alkaloids by Kunze's method gave 1·11 per cent. by the method now described.

An Accra cocoa and a Samoa cocoa gave 3·37 and 3·17 per cent. of total alkaloids, and 3·18 and 2·62 per cent. of theobromine by Wadsworth's method, the caffeine, by difference, thus being 0·19 and 0·55 per cent. Widely differing percentages of caffeine in cocoa are given in the literature. The factor for conversion of nitrogen into theobromine is 3·24, and that for caffeine is 3·46. The factor we have used is 3·26, which corresponds to 10 per cent. of caffeine in the total alkaloid; any variation from the 10 per cent. which would appear to be at all possible would make no significant difference in the percentage of alkaloid found.

Table I gives the percentages of total alkaloids found in six samples of roasted cocoa-nibs of different origins, for the special selection and grinding of which we are indebted to Mr. R. V. Wadsworth.

The Java and Samoa are of the Criollo and the others of the Forastero type. The average alkaloid-content found was 3·10 per cent., calculated on the dry fat-free cocoa-matter.

TABLE I

TOTAL ALKALOIDS IN COCOA-NIBS

Variety	Moisture Per Cent.	Fat Per Cent.	Total alkaloids ($N \times 3{\cdot}26$) on original material Per Cent.	Total alkaloids ($N \times 3{\cdot}26$) on dry fat-free matter Per Cent.
Accra	2·15	55·7	1·42	3·37
Java	2·65	54·0	1·37	3·16
Bahia	2·25	53·8	1·35	3·07
Samoa	3·75	55·6	1·29	3·17
Trinidad	3·10	55·7	1·30	3·16
Grenada	3·01	55·9	1·11	2·70

Table II gives the analyses of five purchased prepared cocoas and chocolate. The average alkaloidal content, calculated on the dry fat-free cocoa-matter, is 3·22 per cent. The average and the variations from the mean are of the same order as those for the unblended nibs.

TABLE II

TOTAL ALKALOIDS IN PREPARED COCOAS AND CHOCOLATE

Sample	Moisture Per Cent.	Fat Per Cent.	Total alkaloids ($N \times 3{\cdot}26$) on original material Per Cent.	Total alkaloids ($N \times 3{\cdot}26$) on dry fat-free cocoa-matter Per Cent.
"S" chocolate* ..	1·2	50·3	1·11	3·19
Cocoa of unknown origin	7·8	25·6	2·32	3·48
Brand A cocoa ..	7·9	25·2	2·31	3·46
,, B cocoa ..	6·5	24·7	2·13	3·09
,, C cocoa ..	3·8	23·4	2·10	2·89

* The sample of "S" chocolate contained 13·7 per cent. of sucrose.

DETAILS OF METHOD.—*Reagents.*—The clarifying agent used is that of the Dutch Codex, adopted by the Society's Milk Products Sub-Committee for the clarification of condensed milk:

Zinc acetate solution.—21·9 g. of crystallised zinc acetate, $Zn(C_2H_3O_2)_2.2H_2O$, and 3 ml. of glacial acetic acid, in water, made up to 100 ml.

Potassium ferrocyanide solution.—10·6 g. of crystallised potassium ferrocyanide in water made up to 100 ml.

The chloroform should be washed with slightly acidulated water. For the alcohol, industrial methylated spirits has been found to be satisfactory.

PROCEDURE.—Grind 2 g. of prepared cocoa or 2 or more g. of cocoa-nib or chocolate to a smooth paste with a little alcohol (80 per cent. V/V), and transfer to a 200-ml. flask with more alcohol of the same strength, sufficient to produce a total volume of about 100 ml. Add 1 g. of freshly-ignited magnesium oxide and digest in a boiling water-bath for 1½ hours under a reflux air-condenser, with occasional shaking. Filter while hot through a small Buchner funnel, return the residue to the flask, and re-digest for half an hour with 50 ml. of the alcohol. Filter and repeat the digestion with a further 50 ml. of alcohol (80 per cent.). Evaporate the combined extract on the water-bath, adding hot water from time to time to replace the alcohol lost. When all the alcohol is removed, finally evaporate to about 100 ml., add 2 or 3 drops of hydrochloric acid (10 per cent. HCl) and transfer the liquid to a 150-ml. measuring flask. Cool, add 5 ml. of the zinc acetate solution and mix, and then add 5 ml. of the potassium ferrocyanide solution. Make up to the mark with water and mix thoroughly by shaking. Allow the flask to stand for a few minutes, and filter through a dry filter paper.

Evaporate a measured quantity (about 120 ml.) of the filtrate to about 10 ml., transfer to a separator and extract by vigorous shaking with five successive 30-ml. quantities of chloroform. Run off the chloroform after each extraction into a second separator, and wash the combined extracts with 3 to 5 ml. of water. Repeat the above process of extraction with five successive quantities of chloroform, wash the second chloroform extracts with the same wash-water, combine the whole of the extracts, and remove the chloroform by distillation. Dissolve the residue in a little hot water, transfer to a Kjeldahl flask, add 0·2 g. of sucrose and 10 ml. of concentrated sulphuric acid. Heat over a small flame till frothing ceases; add 0·02 g. of selenium and digest till colourless. Heat for one hour longer, and determine the ammonia in the usual way by distillation into $N/10$ acid.

Use the factor 3·26 for conversion of nitrogen into alkaloid.

PART II

THE DETERMINATION OF COCOA-MATTER* IN FLOUR CONFECTIONERY

The sale of artificial colouring matters to confectioners for the purpose of making articles of so-called chocolate confectionery has been reported recently.[5] The use of such preparations in foodstuffs would naturally lead to misleading descriptions, since the chocolate could be reduced to very small proportions or omitted altogether. It was, therefore, thought desirable to devise a method for detecting, and, if possible, determining small amounts of cocoa-matter in foodstuffs.

In the analysis of chocolate confectionery, no direct determination of cocoa-matter itself can usually be made. It can sometimes be found by difference after all other substances have been determined, but this method is of very limited application and, indeed, almost useless when searching for small amounts.

Other methods, such as the comparison of the colour of the sample under examination with similar mixtures containing known amounts of cocoa, are still more indefinite, since the tinctorial power of different samples of cocoa varies greatly and depends on the acidity and moisture-content of the final mixture. Fibre estimations are sometimes of value, but are useless when dealing with flour confectionery of uncertain composition. Even very small proportions of cocoa can usually be detected by a microscopic examination either of the original material or of the fibre after treatment with acid to remove starch and sugar, but the quantity present cannot be thus determined.

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* Cocoa-matter is, throughout, assumed to be cocoa-nib and not shell.

On the other hand, assuming an average value for the percentage of alkaloid in cocoa, a close approximation to the amount of cocoa present should be obtainable by a determination of the alkaloid. The reliability of such a method depends on two factors: first the accuracy with which the alkaloids can be determined, and, secondly, the difference in the alkaloid-content of cocoa, due either to natural variation or to manufacturing processes.

With regard to the first, it will be shown later that the amount of cocoa alkaloids in chocolate cakes can be determined as easily, and almost as accurately, as in cocoa itself. Even when very small amounts of alkaloid of the order of 2 mg. have been extracted, the experimental error has not been greater than 10 per cent.

The second factor requires more consideration. Wadsworth,[6] as the result of the examination of many varieties of cocoa-nib, found a variation of from 2·2 to 3·9 per cent. of theobromine, on the dry fat-free basis. Representative manufactured cocoas showed a much smaller variation—from 3·0 to 3·6 per cent. It has been stated that Criollo cocoas contain less theobromine than do Forastero, but no data are available as to total alkaloid.

The varieties of nib, the analysis of which is given in Part I, were chosen so as to exhibit maximum variation, two of them being Criollo and four Forastero.

The total alkaloid varied from 2·7 to 3·37 per cent. The Samoa, which had a low theobromine-content, was not low in total alkaloid, and it may be that a low proportion of theobromine is usually associated with a high caffeine-content.

In the analysis of flour confectionery we take the average figure of 3·15 per cent. for the total alkaloid in dry fat-free cocoa-matter. The extreme variations so far encountered might lead to an error, in the estimate of the proportion of cocoa present, of about one-seventh of the cocoa. When the proportion of cocoa is not large, as is usual in the materials being considered, such an estimate is within ordinary requirements.

The application of the method described in Part I to the analysis of flour confectionery requires certain modifications.

THE NITROGEN DETERMINATION.—The extraction of 20 g. of cake containing 5 per cent. of cocoa would yield about 30 mg. of alkaloid. Such a quantity may be dealt with just as in the case of cocoa itself, but very much smaller quantities of alkaloid than this may have to be determined. Quantities of the order of 2 or 3 mg. are suitable for a micro-Kjeldahl distillation, but in such cases we have used direct nesslerisation of the sulphuric acid digestion solution, after neutralisation. The alkaloid cannot be weighed, owing to the presence of small quantities of impurities.

Two mg. of theobromine were digested with sulphuric acid, sucrose and selenium, and neutralised with soda. By nesslerisation, ammonia equivalent to 2·17 mg. of theobromine was found. Two mg. of theobromine, dissolved in 10 ml. of water, were extracted with three 50-ml. quantities of chloroform, and the residue, on evaporation of the chloroform, was digested as before; nesslerisation gave ammonia equivalent to 2·10 mg. of theobromine. Selenium does not interfere with the nesslerisation. The result must be corrected for ammonia yielded by the digestion reagents.

As an extreme case we have taken a cake weighing 80 g. containing 0·2 g. of cocoa, corresponding to about 4 mg. of alkaloid. The whole of the cake was extracted; about one-sixth of the chloroform extract was evaporated separately, and the residue was shown to contain theobromine or caffeine by the murexide test; the remainder was taken through the process of digestion, etc., with final nesslerisation. The result is given in Table III; 0·25 per cent. of cocoa in a cake can thus be identified and determined.

Volume of Precipitate Correction.—With cakes containing much fat an allowance may have to be made for the volume occupied by the fat in the zinc ferrocyanide precipitate. This can be arrived at by evaporating a portion of the alcoholic extract to expel alcohol, and extracting the fat with a mixture of ether and petroleum spirit. The volume of the zinc ferrocyanide precipitate itself may be neglected.

Results of analyses of cake containing known and unknown quantities of cocoa are given in Tables III and IV.

This method, though primarily intended for flour confectionery, is applicable also to the analysis of various prepared mixed foods containing cocoa.

Table III

Application of the Method to Articles of Known Composition

		Dry fat-free cocoa-matter calculated on		
Material analysed	Total alkaloids found (N × 3·26) g.	the known percentage of alkaloid in cocoa used g.	the assumed percentage of 3·15 of alkaloid in cocoa used g.	Dry fat-free-cocoa-matter known to be present g.
0·2 g. "S" chocolate	0·0021	0·066	0·067	0·070
20 g. plain sponge cake, plus 0·030 g. theobromine	0·0310*	—	—	None
20 g. plain sponge cake .. .. (i)	0·00009	—	—	None
(ii)	0·00009	—	—	
20 g. plain sponge cake heavily coloured with "choc" chocolate	0·00010	—	—	None
20 g. plain sponge cake, plus 2·5 g. "S" chocolate	0·0282	0·89	0·90	0·87
20 g. plain sponge cake, plus 0·2 g. "S" chocolate	0·0022	0·069	0·070	0·070
10 g. chocolate sponge cake prepared in laboratory (contained egg)	0·0039	0·135	0·124	0·140
80 g. chocolate cake containing much fat prepared in laboratory (contained egg)	0·0048	0·166	0·152	0·146

* Equal to 0·0308 g. on theobromine factor.

TABLE IV

APPLICATION OF THE METHOD TO A CHOCOLATE CAKE OF UNKNOWN COMPOSITION

Quantity of cake analysed g.	Total alkaloid found ($N \times 3{\cdot}26$) g.	Equivalent to dry fat-free cocoa-matter g.	Estimated percentage of dry fat-free cocoa-matter in dry matter of the cake	Percentage of dry fat-free sugar-free chocolate in the dry matter of the cake, calculated from factory data
20	0·0159	0·505	3·1	3·6
3	0·0022	0·071	2·9	3·6

Note.—In the above analyses the dry fat-free cocoa-matter is assumed to contain 3·15 per cent. of total alkaloids.

DETAILED PROCEDURE FOR FLOUR CONFECTIONERY.—Moisten 20 g. or other convenient quantity of cake in a mortar with alcohol (80 per cent. V/V) and rub to a smooth paste. Transfer to a flask with the addition of a further 200 ml. of alcohol (80 per cent.), add 2·5 g. of freshly-ignited magnesium oxide and digest for 1½ hours under reflux air-condenser in a boiling water-bath. The flask should be shaken frequently to prevent the cake from clotting. Filter through a Buchner funnel and re-digest the residue twice with 100-ml. quantities of 80 per cent. alcohol. If fat is to be determined, collect the alcoholic filtrates in a large measuring flask, make up to the mark with alcohol, and shake vigorously to maintain the fat in an emulsified state throughout the liquid. Remove an aliquot portion for the determination of fat. Evaporate the remainder on the water-bath to about 100 ml., replacing the alcohol by water. Add 2 to 3 drops of dilute hydrochloric acid. Transfer with hot water to a 150-ml. measuring flask, and clarify with zinc ferrocyanide as described in the method for cocoa, making up to 150 ml. with water.

A larger flask and more zinc acetate and potassium ferrocyanide may be used if the amount of fat is large.

Filter, evaporate a measured quantity of the filtrate to small bulk (10 to 20 ml.) and extract with chloroform. If the amount of alkaloid is small (2 to 4 mg.), three 50-ml. quantities of chloroform are sufficient. Otherwise, extract as previously described.

Reserve a portion of the chloroform extract for the qualitative murexide test.* Distil the chloroform from the remainder, dissolve the residue in hot water, and determine the nitrogen either by digestion and distillation into $N/10$ acid, as with cocoa, or by digestion and nesslerisation. In the latter case add 0·1 g. of sucrose and 3 ml. of concentrated sulphuric acid to the residue in a small Kjeldahl flask. Heat over a small flame till frothing ceases, add 0·01 g. of selenium, and continue heating till colourless and then for half an hour longer. Cool, dilute, neutralise with caustic soda and make up to 100 ml. Determine the ammonia- or nitrogen-content of this solution by nesslerisation. Correct the result obtained for the ammonia-content of the digestion reagents. Use the factors of 3·26 and 100/3·15 for conversion of nitrogen into alkaloid, and alkaloid into dry fat-free cocoa-matter, respectively.

* See also ANALYST, 1935, 200. Theobromine reacts to this sensitive test.

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16 SOUTHWARK STREET
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DISCUSSION

Mr. MOIR, replying to Mr. A. More, who asked whether the cocoa in the test cakes had been mixed with, and baked with, the flour, said that that was the case. In reply to Mr. Grinling, Mr. Moir said that the possible presence of cocoa-matter in the cream-filling of chocolate sandwich had not been dealt with.

Mr. HINKS said that it had been brought to their notice that evening that extensive washing of the cocoa with water or alkaline water was sometimes the practice, the aqueous washing being rejected. This practice might remove a proportion of the alkaloid and might account for a part of the variations found.

Colour Measurement of Oils and Other Liquids

BY E. R. BOLTON, F.I.C., M.I.CHEM.E., AND K. A. WILLIAMS, B.SC., F.I.C.

(*Read at the Meeting, May* 1, 1935)

THE colour of transparent liquids or solids is usually measured by visual methods, that is, the light transmitted through a given thickness of the liquid is compared with that transmitted through standard filters.

The filters are of three "primary" colours, so related that the sensation of white, pure grey or black can be matched by mixing them in suitable proportions.

The matching colour may be obtained either by the use of a graded series of these filters in conjunction with a single light source, as in the Lovibond method; or by combining the light transmitted by varying areas of a single set of filters, as in the Guild system.

The Guild method has been standardised at the National Physical Laboratory and is, undoubtedly, a very satisfactory system, but the apparatus is extremely expensive, and, in consequence, is used in few laboratories.

The Lovibond method is widely used, as the apparatus is comparatively cheap. It gives satisfactory results in the hands of any one observer, but prolonged experience shows that two observers can rarely obtain the same results.

This fault is not one of design and is in no way due to the instrument, but arises from the limitations of the human eye, no two eyes seeing exactly the same. This limitation has caused innumerable differences of opinion regarding the colours of oils and has led to a widespread desire for an instrument which is independent of the variations of the human eye.

Amongst others, R. Toussaint[1] and H. Hirsch-Muller (B. Pat. 415,282) have put forward instruments with which they have attempted to solve the problem, taking the obvious step of using photo-electric cells as substitutes for the human eye.

Hirsch-Muller's instrument involves the use of several vapour-discharge lamps (*e.g.* sodium, thallium and cadmium lamps), and is, in consequence, expensive and somewhat slow in operation.

Toussaint's instrument employs incandescent electric lamps and attempts to obtain light of narrow wave-band by filtering the light through standard coloured filters.

We, also, have adopted the latter principle in investigating this problem, and we claim to have improved considerably upon earlier instruments.

We have found that no infra-red rays from the source of radiation must be allowed to impinge upon the photo-electric cell if true colour measurements are to be obtained. This is particularly necessary when incandescent electric lamps are employed, since such lamps generate a considerable infra-red radiation, and standard filters of the type commonly employed transmit such rays freely.

Accordingly we have devised a method and apparatus whereby we ensure the elimination of the infra-red rays, with or without the elimination of other undesired rays.

IDEAL INSTRUMENT.—The ideal instrument would be one in which a parallel beam of standard white light of given cross-section passed through a coloured filter capable of transmitting only a narrow wave-band, then through a given depth of the liquid, or transparent material, to be examined, and fell on the photo-electric cell, the current or potential difference generated in the cell being measured by suitable means. A blank experiment, in which the liquid was omitted from the beam, would measure the light transmitted by the filter, and the proportion of light transmitted by the liquid would be calculated from these observations. The experiment would be repeated for various wave-bands in order to obtain the transmissions for the whole visible spectrum.

There are thus several apparently important requirements: First, the photo-electric cell must be reasonably sensitive to all visual wave-lengths, and should, preferably, simulate the human eye in this sensitivity.

Secondly, the filters used must transmit the desired wave-band only.

Thirdly, a standard source of white light is desirable.

We have found the Weston Photronic cell (Model 594) to be admirably suited to the work and to fulfil the conditions noted. It is very simple to use, and merely requires to be connected in series with a sensitive galvanometer, no batteries or additional resistances being required.

The current developed is almost exactly proportional to the illumination, if the external resistance is not high, and the galvanometer reading may therefore be taken as a direct measure of the light falling on the cell.

FILTERS.—In our early work we employed the three Ilford trichromatic filters and obtained very encouraging results. In view, however, of the desirability of standardising the apparatus we decided to substitute the three filters chosen by Guild for his instrument. In this way we obtain results based on the same primaries as are used by the N.P.L.

The filters in question, described by Guild,[8] are the Wratten filters Nos. 71A, 49B and 62, manufactured by Kodak Ltd. To these we have added three more filters, in order to cover the whole visible spectrum, *viz.* Wratten filters Nos. 72, 73 and 75.

These filters are probably as satisfactory as any available for the work, but have the disadvantage of transmitting small amounts of light apart from the desired wave-bands—mostly in the yellow or red—and, what is far more serious, they all transmit freely in the infra-red. Now, the photo-electric cell is very sensitive to infra-red radiation, and the electric lamps suitable for use as light sources radiate freely in this region.

We were, therefore, faced with the problem of removing infra-red rays from the light-beam if true measurements of colour were to be obtained, but have accomplished this with complete success by introducing a 2-inch cell filled with 1 per cent. copper sulphate solution in front of the filters. Our observations with infra-red filters show that this depth of solution is sufficient to remove the infra-red rays completely, and also most of the unwanted transmission of the filters in the visual region.

We feel that we have here the greatest advance that we have made in the development of the instrument, and it is not too much to claim that without a filter of this type no photo-electric tintometer can prove successful.

Table I will serve to show the enormous effect produced by the removal of infra-red rays, and will also show that any instrument permitting their passage to the photo-electric cell cannot possibly give a true measurement of colour. The results were obtained in making measurements of the colour of a raw linseed oil contained in a 1-inch cell.

The figures in column A represent the results obtained if light alone be transmitted; those in column B are higher, since infra-red rays are also present and affecting the photo-electric cell.

TABLE I

RAW LINSEED OIL

	Transmission, per cent.	
Nominal wave-band of filter	A With copper sulphate filter	B Without copper sulphate filter
1. 420 to 480$m\mu$ (blue)	0	54
2. 465 to 515$m\mu$ (blue-green)	1	48
3. 515 to 565$m\mu$ (green)	24	77
4. 565 to 585$m\mu$ (greenish-yellow)	46	91
5. 605 to 615$m\mu$ (orange)	45	76
6. 615 to 700$m\mu$ (red)	45	76

LIGHT SOURCE.—In designing his instrument, Guild has paid particular attention to the light source, and has evolved an elaborate method of standardising and correcting it in order to obtain white light. The maintenance of his standards, however, is difficult, as they require continual checking—which is undesirable in a method designed for ordinary laboratory practice.

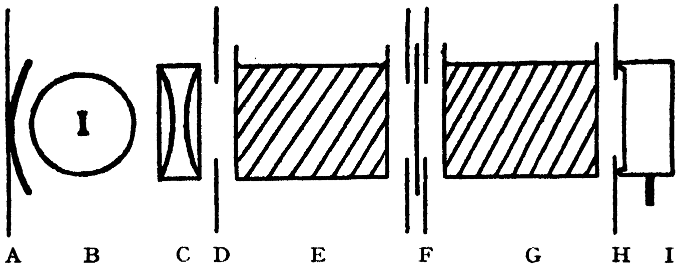
It seemed to us that simplification was absolutely necessary, and we have been fortunate in finding that the standardisation is completely unnecessary if the copper filter is employed in conjunction with the above-mentioned Wratten filters.

Electric lamps operating at almost any colour temperature from about 1500° K to 3000° K can be used if the filaments are sufficiently closely wound, and yield identical results in our instrument. This is due to the efficient operation of the filters in separating the wave-bands required, and to these wave-bands being sufficiently narrow to ensure even lighting over the whole band at each colour temperature.

We have thus removed the necessity for careful standardisation of the light source, and the necessity for employing daylight or something approaching it; and we have substituted for the human eye a device which will give reproducible figures agreeing to within one or two per cent.

Apparatus.—The apparatus we finally evolved is shown (diagrammatically) in Fig. 1 (which is self-explanatory) while a photograph of our own instrument appears in Fig. 2.

Fig. 1



A, mirror; B, lamp; C, condenser; D, stop; E, copper sulphate filter; F, Wratten filter *A*; G, cell with liquid under test; H, stop; I, photo-electric cell connected to galvanometer.

The light source, with its mirror and condenser, is fitted in a box mounted on an optical bench. The copper filter, liquid cell, stops, filters and photo-electric cell are mounted in a second light-tight box on the same bench.

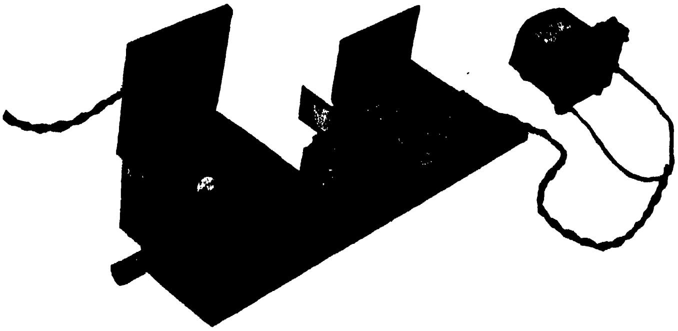


Fig. 2

The apparatus is used as follows:—The light source is connected with the mains by means of a suitable resistance. One of the filters is inserted in the place provided at A, and an empty cell is placed in front of the photo-electric cell (at B [Fig. 1]). Current is passed through the lamp and adjusted to the requirements of the lamp. The system is allowed to stand until this current is steady and the galvanometer deflection is read. The empty cell is replaced by one filled with the liquid under test and the deflection again read. The light-tight box should be closed for both observations.

The percentage of light transmitted by the liquid is obtained by dividing the second of the above readings by the first, and multiplying the result by 100. This figure, subtracted from 100, gives the percentage of light extinguished by the liquid.

The operation is repeated with the other filters, and in this way is obtained a set of six percentage transmissions and extinctions covering the visible spectrum.

Fig. 3
NORMAL OILS
ARACHIS, LINSEED, TEA-SEED, SOYA, SUNFLOWER, SESAME, RAPE

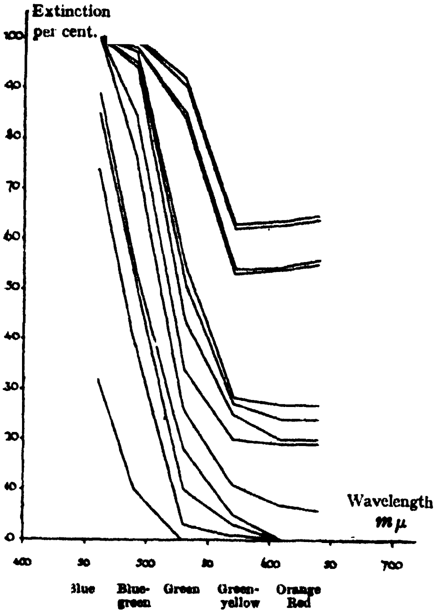
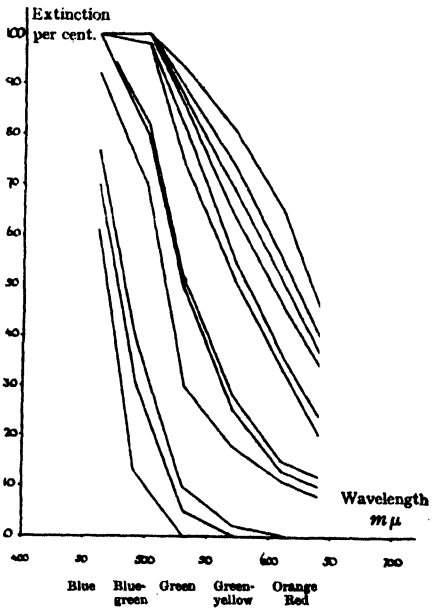


Fig. 4
RED OILS
COD, WHALE, SARDINE, SHARK



APPLICATION TO OILS.—We have made an extended application of the method to liquid oils and have produced a large number of results for oils of varying depths of colour. This has had the object partly of determining how the colour varies from oil to oil and partly of finding a simple method of expressing the results. It seemed to us that a set of six readings for each oil was an unnecessarily complicated way of expressing the colour, and experience has proved this to be so.

We have set out in Figs. 3, 4 and 5, three sets of observations made upon a wide range of oils. Fig. 3 shows the normal oils; Fig. 4 the fish oils, which are reddish in colour; and Fig. 5 a number of olive oils of a greenish colour.

We have found, in addition, a few oils intermediate in character between these three types, but the chief characteristics are clear from these curves. It will be seen that in each set of curves there is a gradual change in the spectral characteristics of the oils as one passes from pale to dark oils, and that this change proceeds in an orderly manner in each type.

The pale oils of each type have almost exactly the same characteristics, and the difference only becomes apparent in the darker oils.

It is clear from the curves that if one knows to which type the oil belongs, the depth of colour is accurately fixed by the extinction or transmission for any filter in the middle of the visible spectrum, and, of these, the figure for the Wratten No. 62 filter is probably the most satisfactory.

Fig. 5
GREEN OILS
OLIVE OILS

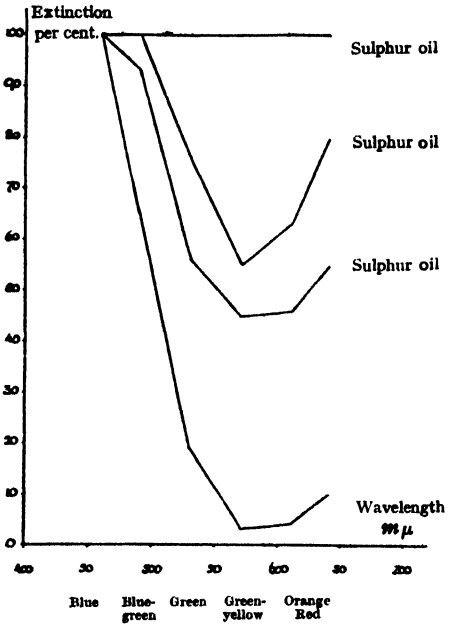
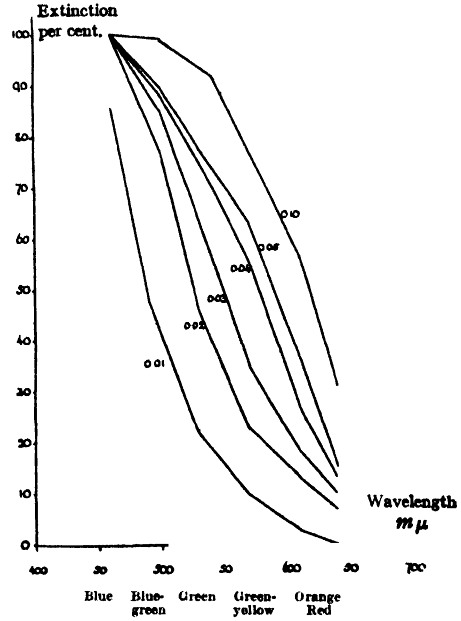


Fig. 6
IODINE SOLUTIONS



If, in addition, the figure for the Wratten No. 71A red filter be considered, information showing the type of oil is obtained, since the variation between the types is fixed by this figure.

It is, therefore, only necessary to measure the extinction or transmission for the green and red filters in order to fix the colour of a fatty oil. The intermediate oils respond equally well to the same treatment.

We suggest that, in using this instrument, the extinctions for the red and green filters should be recorded for each oil examined, and that these figures provide an accurate and reproducible measure of the colour of a fatty oil.

The curves drawn have been obtained by the use of 1-inch oils cells, as we find this depth of oil to be very satisfactory for most oils. In the case of pale oils, however, it is preferable to use a deeper cell, for much the same reasons as prompt its use with visual observations; we accordingly use either 2-inch or 5¼-inch cells where necessary, substituting suitable light-tight boxes for holding the cells.

We have made a number of observations of the colour of oils, in which Lovibond colour readings were obtained in addition to transmission and extinction percentages, and we find that the figures of the two methods are roughly correlated.

This is illustrated in Table II, in which are set out the Lovibond red figures and the corresponding red figures (using Wratten No. 71A filter) obtained by our method. The figures are all for "normal" oils in 1-inch cells.

TABLE II

Liquid under test	Bolton and Williams method Extinction Per Cent.	Lovibond red units
1. Arachis oil	1	0·8
2. Teaseed oil	15	2·0
3. Linseed oil	21	2·4
4. Soya oil	55	4·8
5. Soya oil	65	5·1

The algebraic equation connecting the results of the two methods is different for the other classes of oils, but is equally definite. We hope to publish data regarding this point at a later date.

We believe that our instrument and method offer several advantages:—

(i) More accurate measurements of colour can be made than have hitherto been possible, because the variations of the human sight are eliminated, and readings are reproducible to within one or two per cent. by different observers.

(ii) An accurate standardisation of the source of light is not necessary.

(iii) Readings can be taken very rapidly.

(iv) The results obtained are comparable with those of the best visual methods, although they are obtained in different units.

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6 MILNER STREET
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DISCUSSION

Mr. CHIRNSIDE asked if any precautions were taken to keep the light-source constant.

Mr. MILTON enquired whether fatigue of the photo-electric cell affected the results, as such fatigue might lead to different readings at different times.

Mr. K. A. WILLIAMS, replying, said that the answer to these questions lay in the experimental results. The authors had found that the variations of the ordinary electric supply were insufficient to disturb the galvanometer readings, provided that there was no serious disturbance to the supply in the immediate neighbourhood. Consequently, it was unnecessary to take special precautions regarding the constancy of the light source.

The authors had not found that their results were affected by fatigue of the photo-electric cell. The cells employed did not appear to be seriously affected by fatigue, and in any case the period occupied by blank and test measurements was very short and fatigue was unlikely to be noticeable.

Mr. N. D. SYLVESTER said that he inferred that the instrument had been designed for the measurement of the colour of oils; he presumed, owing to the use of the copper sulphate cell, it would measure any colours of this nature. Had it been tried to measure, say, blue colours? Secondly, had any correction been made for different transmissions? Was the different sensitivity of the cell at different wave-lengths taken into account?

Mr. K. A. WILLIAMS said that any difference in the sensitivity of the photo-electric cell to different wave-lengths could be disregarded, since the desired result was relative and not absolute. It was a known fact that the percentage of light of narrow wave-band, transmitted by a transparent material, was independent of the intensity of the light source—or of the intensity of the light emerging from the material. Consequently, only the relative galvanometer readings (test and blank) for a given light beam were required; the absolute intensity of the beam itself was of minor importance.

The measurements presented in the paper were mostly of yellow and reddish liquids, and the authors had not yet applied their method to blue solutions. They had, however, made measurements of blue Lovibond glasses, and the relation between the various results indicated that the method was quite satisfactory. They hoped to bring some more information before the Society at a later date about this. Meanwhile, he would say that there was no reason why blue colours should not be measured, even if a copper sulphate filter were used. On the other hand, copper sulphate was not the only substance which would cut out infra-red rays; other materials, *e.g.* colourless glass, could be used.

The Use of Infra-Red Rays in the Examination of Inks and Pigments

BY C. AINSWORTH MITCHELL, D.SC., F.I.C.

(*Read at the Meeting, February* 6, 1935)

So far back as 1880 Abney[1] prepared a blue modification of silver bromide which was particularly sensitive to deep-red and infra-red rays, and, using it in a collodion film, he succeeded in taking infra-red photographs. This method, however, was complicated and uncertain, and it was not until the discovery that certain dyestuffs, notably the cyanines and isocyanines, have the property of rendering silver bromide sensitive to infra-red rays that photography at this end of the spectrum became readily practicable, and even then, until a comparatively recent date plates thus sensitised were very unstable. Now that this difficulty has been overcome, new avenues of scientific exploration have been opened and have already led to important discoveries.

The ordinary infra-red plates (Ilford, Afga), when used with the appropriate light-filters, have a sensitivity ranging from about $760m\mu$ to about $900m\mu$, and thus respond also to part of the deep red of the visible spectrum, the limit of which is about $820m\mu$. The infra-red sensitivity may be increased to about $2000m\mu$ by treating the ordinary "I.R." plates with a solution of triethanolamine,* but the range is still only about 0·5 per cent. of the total region of the heat rays. The rays in this borderland beyond the visible red have properties very different from those of the actinic violet and ultra-violet rays. They can penetrate numerous substances relatively opaque to light rays, and, on the other hand, are reflected by certain substances which absorb light. A good illustration of these characteristics is afforded by an infra-red photograph of a summer landscape on a misty day. The rays are not scattered laterally, as are those of light, by the suspended particles of moisture and dust in the mist, but are reflected by the grass and the leaves of the trees, with the result that the photograph appears as a snow-scene with all mist eliminated.[3] These curious effects are apparently related to the phenomena of longitudinal expansion and scattering discovered by Plotnikow.[4] Longitudinal expansion is not confined, however, to the infra-red rays; it belongs also to the rays of the visible spectrum, although in diminishing degree as one passes from the red towards the violet region, but it had not previously been discovered, owing to its photographic effects being masked by the action of the more actinic rays.[*]

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* The method is described by Rawling in his useful little handbook *Infra-Red Photography*, p. 55. See also Baly.[2]

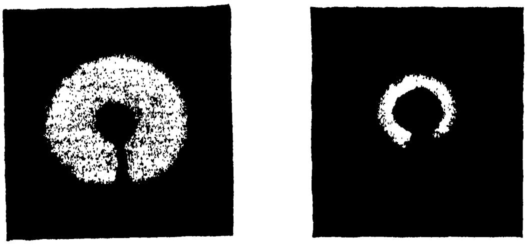


Fig. 2

In certain substances the scattering is so pronounced that some of the rays are bent right round and find an exit in the direction from which they entered (Fig. 3). This reflex scattering, which affords a mechanical explanation of many of the puzzling phenomena associated with heat rays, was established by Plotnikow[6] and his collaborators in a series of quantitative experiments on the skin and parts of the organs of animals. Selective scattering of the rays also accounts for the fact that skiagraphs of the human hand and of a frog can be obtained by the use of infra-red rays, although the outlines are more blurred than in *X*-ray photographs. Herein, too, lies the explanation of the possibility of taking an infra-red photograph of a document within a closed envelope.[7, 8]

[*] THE PLOTNIKOW EFFECT.—The apparatus devised by Plotnikow[5] for proving the longitudinal scattering of visible and invisible rays is shown in Fig. 1 (plate). A beam of light is made to pass through the narrow tube supported by the screen, S, and then through the light-filter, F, to the lens, L, by which it is focussed on the small tube, A, which is closed at one end. Before reaching this point the rays pass through the tube, *d* (here shown detached, but normally supported by the fork, R), then through the spring shutter, V, and the trough, T, and the image of the small tube, A, is photographed on the plate contained in the holder, K, which is provided with movable shutters, *a*, *b*, *c*. If the trough, T, is empty, or contains only water, the image of the tube, A, will not appear upon the plate, but if the tube contains the solution of an organic substance, the image will appear as a dark disc surrounded by a light corona, the extent of which depends upon both the size and complexity of the molecule of the organic substance. For example, with a 5 per cent. solution of starch, 4 mm. thick, through which infra-red rays had passed, an image with a wide corona (*a*) was recorded on an infra-red plate, whereas, after the starch had been hydrolysed with ptyalin for 15 minutes, the scattering of the rays had been greatly reduced and the corona in the photograph was less than a third of the original size (*b*) (Fig. 2). The method may thus be used for studying the progress of enzymic decomposition.

I have to thank Professor Plotnikow for placing at my disposal reprints of papers containing the account of this discovery and its applications, and for sending me a number of unpublished photographs.

In my experience the possibility of thus deciphering the contents of a sealed envelope depends not only upon the relative transparency of the paper, but also upon the composition of the inks upon the document. Printing inks containing lamp-black or Prussian blue are plainly revealed, as is also writing in iron-gall inks, but most red, violet or blue writing or typing inks are usually as transparent as the paper to the rays. Carbon paper is opaque, but a violet paper lining to an envelope affords no protection against an infra-red censorship. In the example shown in Fig. 4 (plate) the black printing ink on the cheque and the blue printing ink of the stamp are clearly brought out, and the signature in blue-black iron-gall ink appears faintly, but the blue ink in which the name of the bank is printed in small characters over the face of the cheque was transparent.

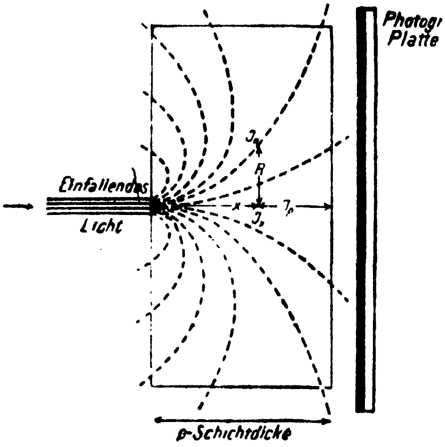


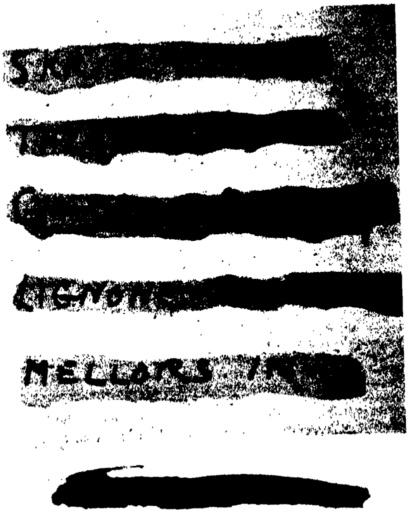
Fig. 3

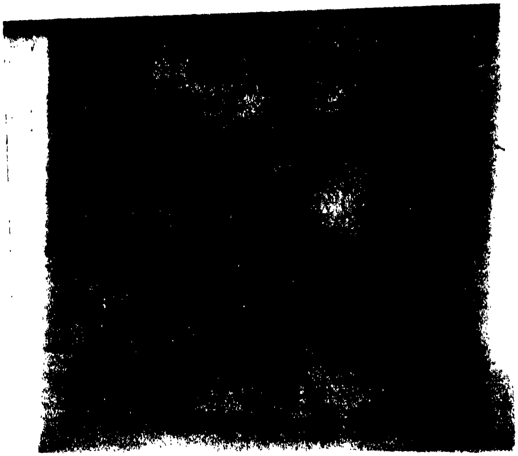
An analogous application of infra-red photography is for deciphering writing or printing that has been obliterated with another ink. The possibility of doing this depends upon differences in the relative transparency of the two inks. Thus if writing or printing in carbon ink has been obliterated with an aniline black or blue-black ink, or with an iron-gall blue-black ink not too rich in iron tannate, the obliterated words are revealed in the photograph.

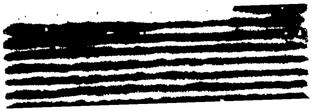
I am indebted to Dr. Bendikson of the Huntingdon Library, California, for a very interesting example of the use of the method in deciphering passages in a copy of the *Collectiones Peregrinationum* by Theodore de Bry (1590–1630), which were expurgated in 1632 by the censor of the Spanish Inquisition (Fig. 5, plate). Chemical tests have not yet been applied to the obliterating ink, but it is probably not a carbon ink, since such inks are relatively opaque to the rays. Contrary to the general belief, however, the opacity of inks containing lamp-black is not absolute, for, by drastic intensification of the infra-red negative, I have succeeded in revealing indications of writing in an iron-tannin ink which had been blotted out experimentally with artists' black carbon ink.

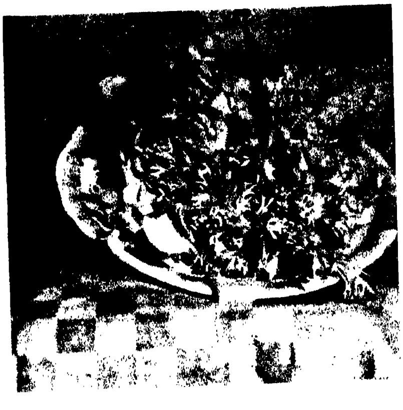
Differentiation of Writing Inks.—The degree of transparency of different inks to infra-red rays depends not only upon the composition of the inks, but also upon their physical properties. Aniline blue-black inks are usually transparent, whilst iron tannate or gallate inks and iron lignone sulphonate inks are more or less opaque, and the two classes may thus be readily distinguished by infra-red photography. The provisional colouring matters—soluble blue and indigo—are practically transparent, and the relative opacity of blue-black iron-gall inks, consisting of a mixture of iron tannates and aniline blue, will usually increase with the proportion of the black iron pigment in the ink. Thus, in a comparative series of tests, in which artists' black ink was obliterated by aniline or iron-gall blue-black inks, Talen's ink (with 0·33 per cent. of iron) was more opaque than "Skrip" (with 0·12 per cent. of iron), and the latter was less opaque than Gimborn's

Fig. 1









ink with 0·2 per cent. of iron. Mellor's ink, containing only a trace of iron, was more transparent than any of the others (Fig. 6, plate).

The relative proportions of blue dye and black pigment in the ink have a greater effect upon the results than the absolute amount of black pigment (as indicated by the iron), and an important physical factor is the way in which, with certain inks, there is differential separation of the blue dye by the capillary action of the fibres of the paper.

Chrome logwood ink is somewhat opaque, and osmium pyrogallate decidedly so, but the common red, blue and violet writing inks are all practically transparent.

In applying the test to a document, care must be taken to compare a large number of strokes of similar density, and it must be borne in mind that the ink in blotted writing will usually contain a relatively higher proportion of blue dye than the ink in unblotted writing. Hence, blotted writing should be compared only with blotted writing, and, even then, only if there are pronounced differences in a large series of strokes can a definite conclusion be drawn that the two inks are different.

So far as my experiments go, there is little difference, if any, between infra-red photographs of strokes in commercial blue-black inks exposed on paper for various periods ranging from 5 minutes to 14 days. Of course, in such inks the iron tannate has already undergone a preliminary oxidation in the vats.

PIGMENTS IN DRAWING INKS.—A systematic series of tests applied to the pigments used for drawing inks, etc., has revealed unexpected differences between them, ranging from the nearly complete opacity of the carbon blacks to the transparency of the vegetable lakes. Between these extremes come pigments with various degrees of transparency, some transmitting the rays through compact layers, whilst others are relatively opaque even in a thin layer. (*Vide infra:* PIGMENTS IN PAINTS.)

SEPIA.—To the latter class belongs the organic pigment, sepia, and it is an interesting fact that the modern sepia derived from the cuttle fish, *Sepia officinalis*, behaves towards the rays in exactly the same way as the pigment from fossil sepia (*Acanthoteuthis* Sp., Oxford clay*). The fact that a natural animal pigment, such as sepia, should be opaque to the rays, whereas the pigment in the skin of a negro apparently reflects them, raises a number of interesting biochemical questions. It is most probable that the human melanin, if isolated, would behave like separated sepia, and that the phenomenon of a negro appearing white in an infra-photograph is another example of the reflex scattering of the rays by living tissue discovered by Plotnikow (*loc. cit.*).

Another significant point about the photograph of a negro is that the reflex scattering does not extend to the pigment in the hairs visible beneath the skin; these absorb the rays. This is also in keeping with the fact that the pigments in dyed or undyed furs (specimens of which were kindly sent to me by Dr. H. E. Cox) behave normally (*i.e.* absorb the rays).

The fact that the pigmentation spots in a frog's skin are relatively opaque to the rays may possibly be due to the skin of an aquatic animal exerting a smaller reflex action upon infra-red rays than does the skin of a terrestrial animal. This hypothesis was supported by an infra-red photograph of a mackerel, in which the black stripes appear as dark as in an ordinary photograph.

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* I am indebted to Mr. Kenneth Oakley for the specimen of this pigment.

Pigments in Paints and Printing Inks.—The yellow pigments used for paints and printing inks are all more or less transparent to the rays: they include cadmium yellow, lead chromate and yellow ochre. Orange antimony sulphide is transparent, and, contrary to expectation, the black modification is also fairly transparent. Of the red and red-brown pigments, alizarine red, scarlet lake, vermilion, cadmium red and red lead are transparent, Indian red is opaque, and red ochre and raw and burnt sienna are transparent, if in very thin layers.

An interesting point in connection with the peculiar transparency of red lead is that the lead oxides appear to be exceptionally sensitive to infra-red rays; it was discovered by Sir H. Davy,[9] so far back as 1812, that exposure of the puce-coloured oxide of lead (presumably lead peroxide) to deep red rays changed it first to red and finally to black.

Analogous differences are to be found in the behaviour of blue pigments. Pure ultramarine, indigo and cobalt blue are transparent, whilst Prussian blue and cyanine blue are opaque. Some commercial specimens of ultramarine, however, are relatively opaque, probably owing to the presence of impurities.

Infra-red photography will thus frequently enable printing inks on documents to be distinguished from one another. Inks containing iron pigments, such as Prussian blue, or violet inks darkened with black ink, will appear dark on the print, whilst most of the red inks and those containing ultramarine and blue lakes will not appear at all in the photograph.

Ancient Egyptian Pigments.—The results obtained with Ancient Egyptian pigments, specimens of which were kindly obtained for me by Mr. A. Lucas, were analogous to those given by modern pigments. Of the yellow pigments, orpiment and two yellow ochres (18th Dynasty) were transparent; red ochre was transparent in very thin layers, as were also azurite and Egyptian blue, but a blue frit containing iron was opaque, and malachite was relatively opaque.

Mediaeval Pigments.—Specimens of azurite, smalt and lapis lazuli from mediaeval MSS. (for which I am also indebted to Mr. Lucas) were all transparent to the rays.

Enamel Pigments.—I have to thank Mr. A. R. Powell and Messrs. Johnson and Matthey for the opportunity of testing a series of commercial mineral pigments. These gave the following results:

Cobalt-nickel-iron black	Opaque
Chrome green (Cr_2O_3 and CoO)	Moderately transparent
Gold purple (Au, 0·25; SnO_2, 2·5 per cent.)	Moderately transparent
Copper green ($CuO.PbCrO_4$)	Nearly opaque
Cobalt blue (CoO, 35 per cent.; ZnO, 40 per cent.; SiO_2, 25 per cent.)	Nearly transparent
Cadmium red (Cd, 60; S, 25; Se 15 per cent.)	Transparent
Cadmium red and barium sulphate	Transparent
Lead-antimony yellow	Transparent
Cadmium yellow	Transparent
Chrome green	Moderately transparent

PIGMENTS IN PENCILS AND CHALKS.—The method is also applicable to the differentiation of the pigments in coloured pencils and chalks. For example, marks made with a blue drawing crayon were transparent, those from a Faber's blue pencil were opaque, and a Duplex blue pencil produced marks that were somewhat transparent.

With copying-pencil pigments the differences in transparency depend not only upon the presence of graphite, but also on the relative proportion of graphite to dye.

Thus the "Swan" copying-ink pencil pigment (which contains no graphite) is transparent, whilst the pigment of Kurz's indelible pencil (with 38·5 per cent. of graphite) is relatively opaque.

MARKING INKS.—The natural vegetable pigments of the Indian marking nut (*Semecarpus anacardium*) and of the berries of the Chinese varnish tree (*Phytolacca clavigera*) are relatively opaque. Infra-red photography, indeed, brings out very clearly the pigment cells in the pericarp of the nut when cut in half (Fig. 7, plate).

Although the pigments in the skins of living fruits and in flowers (Fig. 8, plate) apparently reflect the rays, so that a bunch of grapes appears in an infra-red photograph to be made of wax, it seems probable that the phenomenon is one of reflex scattering associated with proteins, rather than with the pigment itself. This received support from a comparison of infra-red photographs of fresh grapes and dried muscatel raisins, in which the difference in reflection was very pronounced; moreover, a thick layer of chlorophyll is transparent. The black gills beneath a mushroom, however, are opaque to the rays, and have their normal appearance in an infra-red photograph (Fig. 9).

Aniline black marking inks are more or less opaque to infra-red rays, although there is considerable difference in the degree of opacity between markings in two-solution inks (which form the pigment within the fibres) and the one-solution inks, in which most of the pigment is ready-formed. Marking done with silver marking inks tends to be less opaque than that in a two-solution aniline ink.

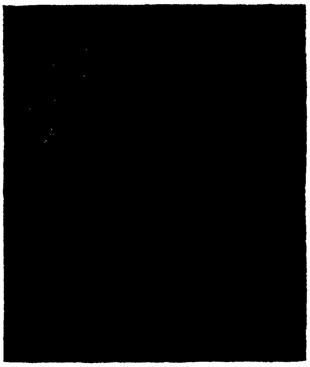

Fig. 9
Infra-red photograph of underside of a mushroom.

THE BEHAVIOUR OF METALLIC SALTS.—Since the salts of various metals enter into the composition of different kinds of inks, systematic tests were made to see what differences could be traced. The principal results were as follows:—

Iron Compounds.—Ferrous sulphate, transparent; ferric sulphate, transparent; ferric sulphate chloride, slightly opaque; ferric salicylate, transparent; ferrous tannate, slightly transparent in thin, opaque in thick, layers; ferric oxide, transparent.

Nickel Salts.—Nickel chloride, transparent; when oxidised, opaque.

Cobalt Salts.—Cobalt sulphate, acetate or chloride (either in blue or pink modification), transparent; cobalt chloride oxidised with hypochlorite, opaque.

Iodine.—A solution of iodine in potassium iodide transmits infra-red rays, and may even be used as a filter in infra-red photography. Starch iodide is relatively opaque.

In each instance the pigment was illuminated with a 60-watt lamp placed 8 inches away. An infra-red light-filter was fixed over the lens, and an exposure of 1½ minute was given at *f*16. The plates were developed with hydroquinone.

EXAMINATION OF CHARRED DOCUMENTS.—Dr. Bendikson has kindly sent me an infra-red photograph of charred paper, the writing upon which had been rendered legible by the use of infra-red rays. My experiments in this direction have met with only limited success. When the charring had not proceeded beyond the brown stage, black pigments, such as the graphite of a pencil or the lamp-black of marking ink could be revealed by the method, but when the paper had become black tinder, only faint indications of writing in pencil or ink, or of characters in printing ink, were obtained. Charcoal is decidedly opaque to the rays. Hence the method does not seem likely to be as generally serviceable for deciphering charred documents as it has been found for reading writing that has become illegible through the discoloration of the material (*e.g.* mummy linen, old leather) through age.

BLOOD-STAINS.—The possibility of using infra-red photography for the detection and demonstration of blood-stains on fabrics depends upon two factors. In the first place the dyestuff in the fabric must be decidedly more transparent to the rays than the oxyhaemoglobin of the blood-stain, and this condition will not often be present. Many dyed fabrics absorb infra-red rays, as was shown by Cunliffe[10] in his systematic study of the relative infra-red reflecting power of pieces of cloth dyed with a series of different dyestuffs. Secondly, the pigment of the blood-stain must be in a condition in which it is relatively opaque to the rays.

In my experience it is possible for a blood-stain, especially one on red material, to be plainly visible to the eye or to appear in an ordinary photograph, but to be invisible in an infra-red photograph. The conditions that enabled Martin[11] to obtain his interesting infra-red photograph of a blood-stain on dark blue cloth must, therefore, have been exceptionally favourable. It might, however, be possible sometimes to overcome the difficulty of contrast by converting the iron of the haemoglobin into Prussian blue, which, as already mentioned, is decidedly opaque to infra-red rays.

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DISCUSSION

Dr. S. O. RAWLING said that he was glad to have the outline of Plotnikow's theory, which was new to him. As he understood it, it was used to explain the "snowy" effect seen in infra-red photographs of such subjects as foliage. Personally, he would rather attribute the phenomenon to the extremely high transparency of chlorophyll; light entering the plant was not absorbed by the chlorophyll, and was therefore scattered in all directions by the cellular tissue.

Dr. Rawling then demonstrated the difference between two green dyes used as inks, and showed how they could be used for secret writing, one of them being opaque, and the other transparent, to rays of about 700$m\mu$. Hence, a secret message written with the first dye and introduced among the words of another message written with the second dye could be revealed by means of infra-red photography or by the use of spectacles containing glass absorbing rays above 700 $m\mu$.

Dr. MITCHELL, replying, said that Dr. Rawling's ingenious method of secret writing also provided an illustration of the way in which the phenomenon of longitudinal and reflex scattering occurred in the visible spectrum as well as in the infra-red region. With regard to the behaviour of chlorophyll towards infra-red rays, the experiments of M. Plotnikow, junr. (*Photographische Korrespondenz*, 1934, **70**, [4], 55), who obtained sharp infra-red photographs when using an alcoholic solution of chlorophyll as the light-filter, indicated that the reflection of infra-red rays by foliage was probably primarily due to the plasma and other substances of high molecular complexity rather than to the chlorophyll. An alcoholic solution of chlorophyll (0·1 per cent.) in a cell, 2 cm. in thickness, showed no material longitudinal scattering, and in this respect it behaved like paper.

Commercial Ground Almonds and their Adulteration

By G. N. GRINLING, F.I.C.

(*Read at the Meeting, April* 3, 1935)

THE most usual adulterant of commercial ground almonds is apricot kernels, and the physical and other constants of almond and apricot-kernel oils are so near to one another as to be almost useless for the detection of adulteration, unless of a gross nature. Several samples of genuine almond and apricot-kernel oils, which I prepared from selected specimens of known types were examined, and the results were as follows:

Type of nut	Iodine value (Wijs)	Sp.gr. at 15·5° C.	Butyro-refractometer reading at 20° C.
Almond (sweet) Barrie	96, 96, 96, 96, 97	0·917 to 0·919	66 to 68
(bitter)	98, 98, 99, 99, 100, 100		
Majorca	101		
Mogador	98		
Palma and Girgenti	97, 98		
Apricot kernels			
Chinese, bitter	104, 106, 107, 107	0·917 to 0·919	66 to 68
Chinese, sweet	102		
Indian, bitter	96		
Indian, sweet	97		
South African	106, 109		

These are all within the range of figures set out in various pharmacopoeias and text-books[1,2,3,4,5,6], *viz.*

	Almond oil	Apricot-kernel oil
Sp.gr. at 15·5° C.	(0·915) 0·918–0·919	0·918–0·919 (0·923)
Iodine value	(93) 95–103·6	(95) 100–110
Saponification value	183, 196(200)	182–192
n_D^{40}	1·4612–1·4642	1·4609–1·4650
Butyro-refractometer reading at 40° C.	56·5–57·5	57·0–58·0

(Figures in brackets are extreme cases.)

In one book[3] it is stated that the average iodine value of 16 samples of ground almonds bought in Bristol in 1921–1922 was 100·5, and that in none was any adulteration detected.

The detection of apricot-kernel oil in almond oil is mainly based upon the results of the Bieber test,[3] which is stated to give a reddish colour with apricot-kernel oil, but little has been said about the sensitiveness of the test. In this laboratory the following modification of the Bieber test is employed:—*Reagent.*—Equal volumes of water and nitric acid (sp.gr. 1·5), free from halogen and sulphur compounds, are mixed together and kept cool during the process.

Bieber test.—Two ml. of the oil are added to 4 ml. of the reagent in a graduated tube, and the mixture is shaken vigorously. In every case pure almond oil has given an upper layer which is not deeper in colour than pale straw, and almost invariably lighter than the oil under test. (The colour depends somewhat on the nature of the almond oil used.) So far, I have not come across a single genuine almond oil which gives even the slightest pink colour by this test, although certain almond oils are said to do so with the Bieber test.[4] In the examination of a large number of commercial ground almonds I have found that the oil gives a brown or amber-coloured upper layer in the test described above; this indicates the presence of a foreign nut, and that, if this is apricot-kernel, the nut must have been treated in some way to evade the Bieber test. It appears that, by comparison with suitable controls, this test is capable of indicating adulteration of genuine almonds with approximately 10 per cent. of apricot-kernel oil, either treated or otherwise.

Lime-water test.—While going through the somewhat scanty literature on almond oil and ground almonds, I came across the following test, which was recommended by de Negri and Fabris.[6] It consists in shaking the oil with calcium hydroxide solution, when apricot-kernel oil gives a permanent emulsion, whilst most other vegetable oils (almond, olive, etc.) remain clear. Preliminary trials with this test indicated that equal volumes of the oil under examination and saturated lime-water (usually 4 ml. of each) were the most satisfactory proportions to use; when the mixture was shaken vigorously and allowed to stand, preferably overnight, genuine almond oil separated in two or three layers or phases, whilst apricot-kernel oil gave a permanent emulsion, and, using these proportions, 15 per cent., and possibly 10 per cent., of apricot-kernel oil could be detected in almond oil. However, as an isolated sample of alleged Majorca almond oil gave an emulsion similar to that given by a mixture of apricot kernels and almonds (a result not obtained with other samples of the same type), it was decided to increase the lime water to 5 ml., with the result, that, whilst the sample referred to did not give an emulsion with this amount of lime water, the sensitiveness of the test was reduced to about 25 per cent.

Up to the present no genuine almond oil giving an emulsion with 5 ml. of lime water has been found, but the oil from certain commercial samples gave an emulsion in this test with both 4 and 5 ml. of reagent, and sometimes a brown layer in our modified Bieber test.

These results have led me to suspect the genuineness of several samples of commercial ground almonds, which are being sold to-day at comparatively low prices.

Most of my work has been done on the oil from blanched nuts of known type, obtained either by expression or by extraction with petroleum spirit. Since this paper was read I have examined Australian and S. African apricot-kernel oils. The former gives an emulsion which is not so pronounced as with Indian or Chinese kernel oils, whilst the latter does not form an emulsion at all.

Although containing definite assertions, this note has also the aim of obtaining opinions upon the results, and co-operation in further investigations.

In conclusion, I wish to express my thanks to Mr. J. G. Foster, Managing Director, British Fondants, Ltd., in whose laboratory this work has been done, for permission to publish this note.

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DISCUSSION

Mr. C. E. SAGE referred to the difficulty of detecting the adulteration of ground almonds with ground peanuts. Apart from the extraction and examination of the oil, there was no definite test; the Bieber test was very unreliable and did not give quantitative results.

Dr. H. E. COX asked how the emulsifying power could be connected with the identity of the oil rather than with traces of fatty acid. In the Bieber test he thought it important to use expressed oil, not extracted oil, as traces of protein matter could produce fictitious results. It was the known practice of some manufacturers to "de-bitter" bitter almonds; what would be the effect of this de-bittering on the almond or its oil in relation to these tests?

Mr. A. L. BACHARACH emphasised the effect of the extracting solvent on the properties of the extracted oil. In a recent paper, for example, it had been stated that the amount of unsaponifiable matter in wheat germ oil varied with the extracting solvent. Whether this were so or not, it seemed highly probable that different solvents would extract different amounts of ether-soluble material, and that this might affect the kind of test Mr. Grinling had been describing.

Mr. GRINLING, replying, said that he had not yet done any work on peanuts, or on the effect of free fatty acids. All his tests had been made on oil expressed from the nuts, usually with a hand-press. With lime water the best results were obtained with small quantities. He felt that the non-fatty portions of the almonds might eventually afford more information than the oil itself.

A Method for the Determination of Small Amounts of Zinc in Commercial Nickel*

By B. S. EVANS, M.C., D.Sc., F.I.C.

For some purposes, notably electro-deposition, zinc is a very harmful impurity in nickel, and it is essential that its amount should be kept below certain limits. The accurate determination of this impurity is, therefore, an analytical operation of considerable importance. Zinc can, of course, be precipitated as sulphide in weakly acid solutions, and in this way separated from small amounts of nickel; when, however, one attempts to carry out this separation from, say, 10 g. of nickel it is found that quite a large proportion of the nickel precipitates also, and to free the zinc from nickel alone requires not one re-precipitation, but several. On the other hand, it is not easy to control the *p*H value of a dark green solution containing large amounts of salts, and, if the *p*H value gets too low, the zinc will be only partly precipitated. From the above considerations it is obvious that there is room for improvement in the standard methods.

The method about to be described is based on the relative stability of nickel cyanide compared with that of zinc, it having been found that zinc sulphide may be thrown down free from nickel by passing hydrogen sulphide through a solution of the cyanides rendered slightly acid with acetic acid. In addition to zinc, commercial nickel and nickel salts are liable to contain a number of other impurities from which the zinc must also be separated; subsidiary operations are therefore described in the account of the process to effect this separation.

Details of the Process.—A sample weight of 10 g. is dissolved in about 100 ml. of dilute nitric acid (sp.gr. 1·2). The liquid is made strongly ammoniacal (dark blue colour and strong smell of ammonia), and is then heated to boiling and allowed to stand. Any ferric hydroxide, etc., is filtered off, washed with dilute ammonia (5 per cent. of strong solution), dissolved in dilute nitric acid and re-precipitated with ammonia; it is again filtered, and the filtrate is added to that from the original precipitation. The mixed filtrates are treated with strong potassium cyanide solution until any precipitate first formed has re-dissolved and the liquid is of a clear orange colour; a scrap of litmus paper is dropped in, and then acetic acid is added until the paper gives a distinctly acid reaction. The liquid is next heated to about 60° C., the mouth of the flask being closed with a rubber stopper carrying a leading tube and an exit tube, and hydrogen sulphide is passed in, heating being continued until the solution boils. The flask is then removed from the burner, the exit tube is plugged, and the liquid is allowed to cool under pressure of the source of the hydrogen sulphide. The zinc sulphide so precipitated should be free from nickel sulphide; it is probably brownish, but this is due to traces of copper and lead, which must next be removed. The precipitate is filtered off, washed with ammonium nitrate solution (5 per cent.) and dissolved through into a beaker by treatment on the filter with cold dilute (1 : 1) hydrochloric acid, followed by boiling dilute *aqua regia* and by washing with hot water; 10 ml.

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* Communication from the Research Department, Woolwich.

of dilute (1 : 3) sulphuric acid are added to the filtrate, and the contents of the beaker are evaporated until the sulphuric acid fumes strongly. The beaker is cooled, 50 ml. of water and 5 ml. of hydrochloric acid are added, and hydrogen sulphide is passed; after standing, the copper sulphide, etc., is filtered off and washed with 5 per cent. ammonium chloride solution, and the filtrate is boiled until free from hydrogen sulphide; about 0·002 g. of lead* dissolved in nitric acid is added, together with 10 ml. of citric acid solution (100 g. dissolved in 200 ml. of water); the solution is made alkaline with ammonia, 5 ml. of potassium cyanide solution (saturated) are added, and the lead is precipitated by the addition of 2 to 3 ml. of a mixture of equal parts of saturated potassium cyanide and 10 per cent. sodium sulphide solutions. The liquid is boiled until the black precipitate has thoroughly flocked out, and then immediately filtered into a flask, and the precipitate is washed with ammonium chloride solution (5 per cent.). The filtrate is then coloured with methyl red and just neutralised with dilute sulphuric acid (1 : 3); it is diluted to about 200 to 250 ml., and 5 ml. of formic acid are added. The mouth of the flask is closed with a rubber stopper carrying a leading tube reaching to the bottom and an exit tube just passing through the stopper; the solution is next heated to about 60° C., and hydrogen sulphide is passed in a rapid stream, heating being continued until the liquid is boiling vigorously. The exit tube is then closed with a rubber cap, the flask removed from the plate, and the liquid is allowed to cool completely under pressure of the source of hydrogen sulphide. When the liquid is completely cold the zinc sulphide, which should now be white (or very pale buff), is filtered off and washed with a 5 per cent. solution of ammonium nitrate; filtration is best carried out through a Gooch crucible containing a very small paper-pulp filter; after washing, the Gooch crucible is placed in a weighed porcelain crucible, and the filter is burned off in a low-temperature muffle, finishing with a short ignition at red heat. When the crucibles are cold, the residue in the Gooch crucible is dissolved through by treating with about 12 drops of dilute (1:3) sulphuric acid and 2 to 3 drops of nitric acid, which are used to rinse down the sides of the Gooch crucible; this is then removed and rinsed with hot water into the other. The solution of the zinc in the weighed crucible is next evaporated as far as possible on the steam-bath, the crucible is transferred to the plate, and evaporation is continued until fumes of sulphuric acid cease to be evolved. The crucible is then placed in an open muffle, not above very dull red heat, and rotated with the tongs for about 20 seconds after sulphuric acid fumes cease to be given off; it is then cooled and weighed as quickly as possible, heating being repeated until the zinc sulphate ceases to lose weight. As the residue appears to be hygroscopic, it is desirable to have the weights for the later weighings ready on the balance before removing the crucible from the desiccator. The last traces of excess sulphuric acid seem to be retained by the zinc sulphate residue with considerable obstinacy, and it may be desirable to correct for them by dissolving the residue in water, adding methyl red and titrating to an orange colour with standard alkali; not more than 1 or 2 drops of $N/10$ alkali should be required, and 0·0005 g. deducted from the weight of zinc sulphate for every 0·1 ml. needed.

The factor for conversion of zinc sulphate to zinc is 0·4050.

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* This excess lead is added to give a filterable precipitate.

RESULTS.—Experimental trials of the method were made on 10-g. samples of commercial nickel to which 0·10 per cent. each of copper, lead and iron, and 0·05 per cent. of bismuth had been added, as well as varying amounts of zinc; as each of the two grades of nickel used already contained zinc, blank tests were carried out, and the results were deducted from those of the experiments.

The following results were obtained:—

Sample	Nickel weight taken	Zinc added	Weight of $ZnSO_4$ found	Zinc found total	Per cent. of zinc	
					Added	Found (corr.)
	g.	g.	g.	g.		
A	10·0	Blank	0·0034	0·0014	—	—
A	10·0	0·010	0·0278	0·0113	0·100	0·099
A	10·0	0·002	0·0090	0·0036	0·020	0·022
A	10·0	0·005	0·0160	0·0065	0·050	0·051
A	10·0	0·050	0·1260	0·0510	0·500	0·496*
B	10·0	Blank	0·0040	0·0016	—	—
B	10·0	0·020	0·0542	0·0219	0·200	0·203

* In this determination a few drops (say 0·5 ml.) were lost out of a total bulk of 100 ml.

Carried out as described above, the process does not seem to present any pitfalls; attention may, however, be drawn to one fact which seems to have escaped general notice. When a fairly large excess of acid is added to a solution of the double cyanide of nickel, and especially if the liquid is heated, a white insoluble nickel compound, probably analogous to Prussian blue, is precipitated; the formation of this compound is hindered by keeping the acidity low and by the presence of the ammonium salt of the acid. For this reason it is desirable, in the process, to add a fairly large amount of ammonia in first making alkaline, and not to add more acetic acid than is required to give a distinctly acid reaction in acidifying before the first hydrogen sulphide precipitation; for the same reason any prolonged boiling during this precipitation is to be avoided. It is only fair to add that no case of this interference has been encountered, and, in any case, the precipitated double cyanide being insoluble in acid, no nickel should contaminate the zinc after the zinc sulphide has been dissolved off the filter.

The separation from lead is based on the fact that zinc sulphide, while precipitated in the presence of not too large an excess of alkali cyanide, is held in solution if an excess of ammonium salts is present; these two reactions, taken in conjunction, seem to be almost, or quite, specific for zinc. As ammonium cyanide is decomposed with considerable rapidity on boiling, it is not desirable to boil the liquid longer than just sufficient to render the lead sulphide filterable. A note of warning should be sounded with regard to danger of contamination of alkaline cyanide solutions by zinc dissolved from the glass. Almost all resistance-glass contains large amounts of zinc, and in the course of other work I have experienced considerable trouble, which was eventually traced to zinc dissolved from the glass by boiling alkaline cyanide solution. This difficulty does not occur in the process given here, as the alkaline cyanide liquid is cold and is immediately acidified with acetic acid.

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

ALUMINIUM AS AN INDEX OF SOIL CONTAMINATION

In the summary of my work (Analyst, 1934, **59**, 565) it is not made sufficiently clear that the main object of the paper was to show the use of the determination of aluminium as an index of soil contamination. The principle involved depends upon the fact that grasses and clovers invariably absorb only traces of aluminium, and hence if more than traces of alumina (0·025 per cent.) are found in the herbage sample, soil contamination is indicated.

The presence of contaminating aluminium may interfere with the exact determination of traces of such elements as iron, manganese and iodine, which occur to a much greater extent in soils than in herbage, so that even traces of contaminating material may add very considerably to the amounts reported in the analysis of mineral-content.

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Wellington, New Zealand

A RECOMMENDED STANDARD PROCEDURE FOR MEASURING THE COLOUR OF OILS

There appears to be a definite demand among chemists, producers, dealers, and users of vegetable and fish oils for the adoption of a standard method of estimating and specifying the colours of these oils. There is general agreement that there is no difficulty with the light-coloured oils, as satisfactory matches can be obtained with the Lovibond Tintometer, and reasonable agreement reached by observers working in different laboratories. The difficulty arises when the colour readings exceed, say, 20 units in the yellow scale. It is a well-established fact that few observers, particularly male observers, have a keen appreciation of differences in saturation of yellow above 20 units. Reference to the text-books on the Tintometer by the late J. W. Lovibond and to literature subsequently published by the manufacturers definitely recommends restricting colour estimations, wherever possible, to readings below 20 units.

Unfortunately the practice of testing oils in cells 5¼ inches in length has become the general practice of those engaged in the industry. Most oils, when viewed in a length of 5¼ inches, give readings seldom less than 30·0 yellow, and frequently as high as 70 units of yellow, which is much too dark for observers to match correctly.

The practice of using the 5¼-inch cell originated in America, where the colour of cottonseed oil is tested by looking down through the standard sample bottles, which are approximately 5¼ inches in length. It will, however, be unfortunate if the industry in this country is to be bound by the mistaken custom of America.

The procedure we have always recommended is that the samples giving readings higher than 20 units in any one series shall be transferred to a cell of smaller size and the colour reported as made in a cell of that particular size. Admittedly it would be confusing to have colours reported in cells of varying size from different sources, particularly since the reading in a 1-inch cell is not double that of a ½-inch cell, owing to the fact that substances have their own specific rate of light absorption and colour development. This difficulty, however, could be overcome by specifying that, say, a 2-inch cell shall be used, but that if the colour exceeds 20 units in yellow, the sample shall be tested in a 1-inch cell, and if the colour still exceeds 20 units in yellow, the sample shall be tested in a ½-inch cell, or by some other similarly agreed method.

Another cause of error between different observers is due to the different sources of light used in various laboratories. This point could profitably be agreed upon.

We would willingly co-operate with any organised body representative of the industry in defining the most suitable and convenient procedure to be followed in the future.

G. S. FAWCETT

THE TINTOMETER LIMITED
THE COLOUR LABORATORY
SALISBURY

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY PALATINE OF LANCASTER

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1934

OF the 5233 samples examined, 1972 were taken informally.

WEAK ACETIC ACID.—A sample, sold as "weak acetic acid," was found to consist of 33 per cent. acid, which is the "acetic acid" of the British Pharmacopoeia. The strongest acid in the B.P. is described as "Glacial acetic acid." The description applied to this sample "weak acetic acid" might be assumed to be equivalent to the "dilute acetic acid" of the B.P., which contains only 6 per cent. of acid. The vendor's notice was drawn to the composition of the sample.

IODINE PAINT.—A sample, described on the bottle as "Iodine Paint (Methylated)," contained 2·2 per cent. of iodine and 1·5 per cent. of potassium iodide. There is no definite standard for "Iodine Paint," but no formula has been found suggesting an iodine-content of less than 2·5 per cent., whilst most are considerably higher than this. The sample was reported to be at least 12 per cent. deficient in iodine, and, as the sample was an informal one, the vendor was cautioned.

MAGNESIA.—During the year six samples described as *magnesia* were submitted· Three consisted of magnesium oxide, and the other three of magnesium carbonate. Notwithstanding the popular idea that *magnesia* denotes magnesium carbonate, official requirements are quite definite that the name is applicable to the oxide and not to the carbonate. In the revision of the B.P. Codex for 1923 it is stated that "It was the practice to refer to the carbonate as magnesia and the oxide as calcined magnesia. The practice when 'magnesia' is asked for is not uniform. In the majority of cases what is intended and is supplied is the light carbonate." This has been deleted from the 1934 revision of the Codex, and the 1932 revision of the B.P. has dropped the synonym calcined magnesia for the oxide, which was contained in the 1914 revision. In view of the want of uniformity in practice, it would be desirable for all the parties concerned to agree.

G. D. ELSDON

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

EXCESS OF SOLUBLE CHLORINE IN RAG FLOCK FROM HESSIAN

Rag Flock Act

On May 23rd a rag flock manufacturer was summoned at the Bury Borough Police Court for having manufactured rag flocks which did not comply with the standard of cleanliness required by the Rag Flock Regulations, 1912.

The Public Analyst (Mr. T. R. Hodgson, F.I.C.) reported that the sample submitted to him contained 475 parts of soluble chlorine per 100,000, *i.e.* 16 times the quantity allowed by the standard.

The defendant admitted the accuracy of the analysis, but contended that the material sampled by the Chief Sanitary Inspector was hessian, not rags. This hessian was made into wadding for use in slippers, and was not used for the bedding and upholstery trades.

Mr. T. R. Hodgson, giving evidence, said that it was unquestionable that parts of the sample he had analysed were made from sacking. In cross-examination he admitted that it was quite possible for a piece of sacking to get accidentally into a machine, but that the material instantly became rag flock.

Professor W. E. Morton, Professor of Textile Technology, Manchester University, said that he had examined part of the sample and that there were at least four pieces of sacking present. In cross-examination he said that samples of rag flock in a case now pending against four Manchester rag flock manufacturers were also made in part from sacking. These manufacturers had received rag flock from the defendant in the present case.

The Magistrates imposed a fine of £10 with £5 15s. costs.

(*Cf.* Analyst, 1924, 49, 430; 1929, 54, 157.)

The National Physical Laboratory

REPORT FOR THE YEAR 1934*

During the year 1934 continued progress has been made in all sections of the work carried out by the Laboratory, and there has been an increased demand for industrial investigations. The increase has been most marked in the work called for by the shipbuilding industry. The much greater attention that has been given throughout the country to the subject of noise has materially increased the work done by the Sound Division of the Physics Department.

Standards of Measurement.—Continued progress has been made with investigations on fundamental standards in the appropriate departments of the Laboratory.

International Temperature Scale.—The work has been mainly concerned with the measurement of temperatures in the upper part of the scale. Attention has been given to the means by which the accuracy of observations with thermo-couples can be improved, and the possibilities of the employment of high precision resistance thermometers have been investigated. At higher temperatures the behaviour of the optical pyrometer has been considered, and re-determinations of the melting-points of platinum and palladium have been made. The results agree well with recent determinations at other national laboratories. The value for platinum was 1773·3° C., and that for palladium about 1555° C.

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* Department of Scientific and Industrial Research. H.M. Stationery Office, Adastral House, Kingsway, London. Pp. 260. 1935. Price 13s. net.

Photometric Standards.—Further work on the establishment of a primary standard of light, based on black-body radiation at the freezing-point of platinum, has been carried out. The method adopted follows closely that proposed by the National Bureau of Standards at Washington, and results agreeing well with those of that institution have been obtained.

Wave-length Standard of Length.—A complete account of the definitive determinations of the yard and metre in terms of the wave-length of the cadmium red radiation, both in air and *in vacuo*, has been published (*cf.* ANALYST, 1933, **58**, 404).

Board of Trade Standards.—The re-determination of the relationship between the pound and the kilogram was completed early in 1934. The resulting value was found to be:—1 pound = 453·592,388 grams.

This value agrees very closely with that obtained in 1922, but both values are smaller by 1 part in 5 millions than the value determined in 1883, which is still used as the legal basis of conversion from pounds to grams or *vice-versa*. Steps are being taken to obtain international acceptance of the value determined in 1933–34.

Volumetric Glassware and Hydrometers.—The Laboratory assisted in the preparation of the "Report on Standard Temperature of Volumetric Glassware," published by the B.S.I. as Report No. 554. A new edition of the Laboratory test pamphlet, "Tests on Volumetric Glassware," was published in 1934. (*Cf.* ANALYST, **59**, 550.)

The value of mixtures of xylene and tetrachloroethane as liquids for use in testing hydrometers has been confirmed, and the Laboratory Standard hydrometers, covering the range 1·200 g. per ml. to 1·250 g. per ml., have been reverified by the use of these mixtures.

PHYSICS DEPARTMENT.—Various investigations have been carried out in conjunction with other departments, and for scientific associations, etc. The co-operation of the Laboratory was sought by H.M. Office of Works in finding appropriate housing conditions for paintings, museum pieces and books, from the point of view of the correct methods of humidity control in conditioning the air of museums, picture galleries, etc.

Work for Food Investigation Board.—Attention was directed to the investigation of humidity measuring instruments at low temperatures and to the preparation of tables for the wet and dry bulb hygrometers at air temperatures down to −20° C. The study of heat-loss from metal pipes in an air-stream has also been continued. The evaporation of water from a plane horizontal surface subjected to a tangential wind-stream has been studied, and it has been found that the rate of evaporation is not proportional to the area of the surface, but is proportional to the width, except for narrow surfaces and low wind speeds.

RADIOLOGY DIVISION.—The *X*-ray studies of the effect of cold work on the structure of metals have been carried to a further stage. A pamphlet describing the nature of the information to be obtained by *X*-ray analysis, and the possibilities of the method has been published (see ANALYST, 1934, **59**, 487).

Structure of Tooth Enamel.—At the request of the Medical Research Council further *X*-ray studies of the structure of tooth enamel have been carried out. This work suggests the possibility of a classification of various types of enamel, based on the nature and extent of the fibre structure or selective crystal orientation which characterises the enamel and distinguishes it from the underlying dentine.

National Radium Standard.—The British national radium standard, for over 20 years in the possession of the Laboratory, has been replaced by a new standard of exceptionally pure radium chloride. A comparison shows that the value of the radium-content of the old standard, based on that of the new, agrees within about 0·3 per cent. with the figure derived from the original certified value, after allowing for radioactive decay during the period 1912–1934.

ENGINEERING DEPARTMENT.—Steady progress has been maintained with the various items of general research and in the special investigations for different authorities. Of the new researches begun during the year, mention may be made of the investigation of the lubricating value of synthetic oils derived from coal. The investigation into the methods of testing thin sheet metal has been completed.

The curious effect of atmospheric corrosion during the fatigue of metals has been traced to the presence of water vapour, and has been shown not to be due to atmospheric impurities.

METALLURGY DEPARTMENT.—*Alloys of Iron and Carbon.*—In the course of the work it has been found that pure alumina, which is not acted on by molten iron, is reduced to some extent by molten alloys of iron and carbon, and it has therefore been necessary to devise a method of lining crucibles and of coating thermo-couple tubes with thoria in order to prevent this action. Although the amount of aluminium taken into the iron in this way is very small, it is important that the metal used should be of the highest possible purity.

Light Aluminium and Magnesium Alloys.—Certain of these alloys present great difficulties in forging from the cast state, although after the original cast structure has been broken down, working can be carried out satisfactorily. These difficulties have been largely overcome by a method of slow pressing at a high temperature.

Steels at High Temperatures.—Further modifications have been made in the apparatus for the study of the creep of steel at high temperatures *in vacuo*, and good progress has been made with the examination of such specimens under different loads and at various temperatures. The steels used in the research have also been exposed to the action of superheated steam in a high-pressure vessel, and the mechanism of corrosion has been studied.

Action of Carbon Monoxide on Steel.—In the course of the work on gas cylinders for high pressures, attention has been called to the action of carbon monoxide on the steel, considerable quantities of liquid iron carbonyl having been found in some cylinders under these conditions. Some attack on the surface, causing minute flaking, has been found, but no evidence of inter-crystalline cracking caused by carbon monoxide has been observed.

Steel cylinders that had been used for the storage of compressed coal gas for periods of 12 months or longer have also been examined. Some of these showed definite signs of corrosion of the internal surface, and in at least one instance an appreciable amount of foreign matter was present. The deposit consisted of organic matter, with iron and sulphur. Microscopical examination showed that the corrosion partly took the form of preferential attack along the grain boundaries.

ELECTRICITY DEPARTMENT.—Work on absolute electrical measurements has been continued. In the Photometry Division work on precise candle-power and flux measurement is still in progress, and the characteristics of the comparatively new form of photo-electric cell known as photovoltaic rectifier or contact cell have been investigated.

Plumbo-solvency.—The investigation of plumbo-solvency has been continued in conjunction with the Chemical Research Laboratory. The general results indicated that the greatest voltages or currents that were likely to occur in pipes in service would not cause any significant amount of lead to pass into the water carried, if the pipes were of reasonably low electrical resistance throughout. If the electrical resistance at a joint were sufficiently high—much higher than is likely to be the case in practice—electrolytic action might occur, and lead pass into the water. In general, however, this would be detected by the existence of a serious leak.

Ceylon

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1934

THE Government Analyst (Mr. J. A. V. Collins) opens his report with a tribute to the work of his predecessor, Mr. C. T. Symons, who resigned in September, 1934, after 22 years' service.

The work done during the year involved the examination of 2462 articles and 1510 reports. These were largely concerned with criminal investigation work (1665 exhibits), examinations of liquors were made for the Excise and Customs, and 431 samples of milk were analysed. Of these, 276 were adulterated—a record number. The increase of adulteration is attributed to the shortage of milk caused by the exceptionally dry conditions over a large part of the year. Several samples contained diluted, sweetened condensed milk. The highest amount of added water recorded was 73 per cent.

In the criminal investigation work several points of interest are recorded.

DETECTION OF ASPIRIN IN URINE.—In connection with a murder trial, experiments were made with aspirin and chloroform. Urine was collected from patients who had been treated with 15 grains of aspirin. One sample was preserved with formalin; to the other nothing was added. Salicylic acid was readily identified in both samples after standing for 14 days.

A cat which had been chloroformed was preserved by formalin injection. After 28 days a post-mortem examination was made, and chloroform was identified by Ragsky's method in the liver and in the blood.

ABORTION DRUG.—A drug recommended in a case of abortion was found to consist mainly of potassium nitrate and saffron.

FISH POISON.—In connection with a case of alleged fish poisoning it was found that the bark of the mahapatta tree (*Lasiosiphon eriocephalus* Decne. var. *Zeylanicus meissn*) is toxic to fish.

CLOTH USED AS GUN WADS.—In several cases it was possible to show that small pieces of cloth used as gun wads in muzzle-loading guns, and picked up at the scene of the crime, had actually been torn from old pieces of cloth found in the houses of suspected accused.

Straits Settlements

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1934

IN his annual report the Government Analyst (Mr. J. C. Cowap, B.Sc., F.I.C.) gives an outline of the general work of the Department carried out in the Laboratories at Singapore and Penang. The greater portion of this work is provided by the Monopolies Department, and is concerned with the assessment of duty, the protection of revenue, the purchase of chandu dross, and the supervision of the quality of toddy sold in Government toddy shops. The Government Analyst is in charge of the Opium Factory and is responsible for the quality of its products.

From the Medical Department are received toxicological and clinical specimens, drugs and chemicals, drinking water, and some foods.

From the Police Department are received exhibits in any cases of crime in the investigation of which chemistry may be an aid.

Among items of interest, to which attention is directed, are the following:—

CHANDU DROSS.—Opium, as prepared for smoking, is termed chandu. It is manufactured from raw opium by successive processes of roasting, extraction with water, filtration, evaporation and fermentation. During these operations considerable changes occur, notably a loss of alkaloids other than morphine, and the product finally obtained is a dark brown viscous liquid containing from 20 to 25 per cent. of water.

Chandu dross is the residue left in the opium pipe after smoking. It is a dry, black granular mass which still contains about 6 per cent. of morphine. It can be re-prepared and smoked again, but, as the smoking of dross is generally held to be more deleterious than the smoking of chandu itself, the Government purchases it from smokers at the rate of $7 per tahil (1 tahil = 1⅓ oz.). During the year 1934 the number of packets of dross valued on purchase from smokers was 7561, and in 3091 of these the morphine was determined.

TODDY.—Toddy is the sap drawn from the unopened flower spathe of the coconut palm. When fresh it contains about 17 per cent. of solid matter, of which 85 per cent. is sugar. It rapidly ferments until it reaches a maximum of 6 to 7 per cent. of alcohol and a minimum of 2 to 3 per cent. of extract (*cf.* ANALYST, 1932, **57**, 627). When the limit of alcoholic fermentation is reached the toddy is acid and stale, and the object of analysis is to ensure that the purchaser will receive a wholesome alcoholic drink. The number of samples of the deliveries to the Government Toddy Shops examined during the year was 2950. During the first six months the quality of the liquor supplied in Singapore was uniformly good, but during the latter part of the year the toddy was frequently grossly over-fermented.

DELETERIOUS DRUGS.—Thirty-eight samples were examined in cases of suspected possession or importation of deleterious drugs. The drugs found were cocaine, Indian hemp and opium. In a few cases cocaine hydrochloride was found to be adulterated with novocaine or a similar synthetic substitute, and in one instance it had been almost entirely replaced by a mixture of phenacetin and caffeine, and in another by wheat flour.

CAUSTIC SODA POISONING.—Of the 45 specimens of viscera and 93 of stomach washings examined, alkali was found in no fewer than 19—an indication of the extent to which caustic soda or strong solutions of sodium carbonate are taken by accident or with suicidal intent. In Cyprus, caustic soda is now a scheduled poison (*cf.* ANALYST, 1935, 180), and recommendations have already been made that it should be placed upon the Poisons List in the Straits Settlements.

IDENTIFICATION OF CIGARETTE ASH.—It was desired to know whether cigarette ash upon the clothing of a woman, who was found lying dead upon a bed, could have been derived from the cigarettes which she habitually smoked, or from the kind usually smoked by a person who was suspected of being concerned in her death. It was proved that the ash was not derived from the woman's cigarettes, but was indistinguishable from the ash of the cigarettes of the suspected person.

Commonwealth of Australia

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

Division of Forest Products*

NO. 14. THE CHEMISTRY OF AUSTRALIAN TIMBERS. PART 4 A STUDY OF THE LIGNIN DETERMINATION, II

IN carrying out this determination by the sulphuric acid method (*cf.* ANALYST, 1932, **57**, 103) it is desirable first to remove extraneous matter. For many woods of the genus *Eucalyptus*, existing methods are inadequate, because these extraneous substances, which resemble "kinos," occur in the cell cavities and are not easily removed; they are not hydrolysed by acid, and consequently figure as lignin.

Different methods of purification are now compared, and it has been found that treatment of the powdered sample with 0·125 *N* sodium hydroxide solution at 98° C. for 1 hour removes also a small amount of lignin. When, however, the residue from this process is subjected to a more prolonged digestion (up to 16 hours) with the alkali, the loss in lignin is very small, and it is therefore concluded that two types of lignin may be present, the major portion being almost insoluble in the alkali. The extracted material may be removed by filtration on a tared alundum crucible, washed in succession with hot water, 30 ml. of 5 per cent. acetic acid, and hot water, dried at 105° C., and weighed.

If consistent results are to be obtained by this method, it is important to consider the amount of the extractive in relation to the volume of alkali used. Thus, where the former is small, 100 ml. should suffice to extract 2 to 2·5 g. of wood, but when it exceeds 35 per cent. 300 ml. are necessary.

Extraction with a hot mixture of alcohol and benzene for 24 hours, followed by hot water (*cf.* Sherrard and Harris, *Ind. Eng. Chem.*, 1932, **24**, 103; Ritter, Seborg and Mitchell, *id.*, 1932, **24**, 1285; *Ind. Eng. Chem. Anal.*, 1932, **4**, 202) does not remove all extraneous substances, particularly when waxy and other substances which may be rendered insoluble are present; the methoxyl value of the lignin obtained has therefore been used to estimate the maximum true lignin-content. This "true" figure is, in many cases, closer to the uncorrected value obtained after alkali-treatment than to that obtained after extraction with the mixed solvents, and the former method is therefore preferred. Rock maple (*Acer* sp.) and *Pinus radiata* (sapwood) contain little, if any, extraneous material, and are therefore not comparable with the eucalypt woods. *E. diversicolor* (Karri), which is also exceptional in several other respects, gives lignin figures, after extraction with the mixed solvent and with alkali, which are 2·1 per cent. higher and 4·5 per cent. lower than the "true" figure, respectively; there are no other exceptions among the eucalypt woods.

Alternative methods, involving the use of alcohol or ether followed by hot water, are being investigated, particularly as the previous objection to the use of alcohol (*viz.* the removal of acetyl groups) has been overcome (*cf.* Ritter and Kurth, *Ind. Eng. Chem.*, 1933, **25**, 1250). Promising results have also been obtained by extraction with alkali for 1 hour, after which acetic acid is added until there is an excess of 3 per cent. After a further hour at 98° C. the mixture is filtered, and the residue is washed in the usual way.

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* Technical Paper, No. 14, 1934, pp. 20; and No. 15, 1935, pp. 24. By W. E. Cohen.

No. 15. IDENTIFICATION OF WOOD BY CHEMICAL MEANS. PART 2 ALKALINITY OF ASH AND SOME SIMPLE CHEMICAL TESTS FOR THE IDENTIFICATION OF THE COLOURED WOODS OF THE GENUS *EUCALYPTUS*

DETERMINATION OF THE ALKALINITY OF THE ASH.—With unknown samples the burning-splinter test (*cf.* ANALYST, 1932, **57**, 101; 1933, **58**, 345) is a useful guide and will divide woods into two categories, *viz.* high and low alkalinity, there being a carbon tip and no appreciable ash in the latter case. Raspings of the sample which have passed a 20-mesh sieve are dried at 105° C. and 2 and 15 g., in the respective cases, are weighed into a platinum dish and ignited in a muffle-furnace at 500° to 600° C. The ash is heated on a hot-plate for 10 minutes with a measured excess of 0·1 *N* sulphuric acid (10 to 20 ml.), and the mixture is then cooled and titrated with 0·1 *N* sodium hydroxide solution, with phenolphthalein as indicator. The results are expressed as ml. of 0·1 *N* acid per g. of oven-dry wood. They should be accepted only if approximately one-half or less of the added acid is consumed, and only sound true-wood should be used.

RESULTS.—The total number of authentic samples examined was 540, and the mean, maximum and minimum values, and the frequency and variation for each of the 37 species concerned are tabulated. In general, the woods may be placed in two main groups according as the alkalinity values are above or below 0·30. Six woods (*E. botryoides*, *corymbosa*, *crebra*, *longifolia*, *rubida*, and *saligna*) gave values in both categories, and two samples of *E. microtheca* (coolibah) from W. Australia gave the exceptionally high values of 28·9 and 41·0.

SIMPLE CHEMICAL TESTS.—Extracts are prepared as follows:

(i) The raspings (5 g.) are digested with 100 ml. of water at 98° C. for 2 hours, the mixture being then filtered on a Buchner funnel and the residue washed with sufficient hot water to give a total filtrate of 100 ml. The extract is then diluted 10 times, if necessary.

(ii) The residue from (i) is re-extracted several times with hot water, and the final residue is dried in air and digested with 80 ml. of alcohol for 1 hour under a reflux condenser. The mixture is filtered, and the residue is washed with alcohol until the cold filtrate amounts to 100 ml.

(iii) The residue from (ii) is re-extracted several times with alcohol and dried, and is then re-extracted with 80 ml. of 0·125 *N* sodium hydroxide solution for 1 hour at 98° C. After filtration, the filtrate is adjusted to 100 ml. with the hot water washings, and 10 ml. are diluted to 100 ml. with water. This solution is made slightly acid with acetic acid and then slightly alkaline with ammonia, excess of the latter being removed by boiling, and the final volume is adjusted to 100 ml.

(*a*) *Ferric chloride test.*—To 2 ml. of extract (i) (undiluted if necessary) are added 3 drops of a 1 per cent. solution of ferric chloride in ethyl ether. The mixture is shaken, and the nature of any colour (blue with "depside" tannins or green with "catechol" tannins) or precipitate is noted. Only 5 woods gave a green colour (*cf. infra*); the colour produced by *E. diversicolor* was different from those from the other four, and was probably due to the presence of unusually large quantities of soluble acid substances, since the tannin-content is known to be very small.

(*b*) *Transient-colour test.*—To 2 ml. of extract (i) are added in succession 1 drop each of 1 per cent. ammonia and 1 per cent. potassium ferricyanide solution. With the exceptions of *E. longifolia* and *E. sideroxylon*, all woods give consistently either a purple or a pink transient colour, or (for woods which give a green colour with ferric chloride) no transient colour.

(*c*) *Dilution test.*—To 2 ml. of extract (ii) are added 2 ml. of water, and the degree of turbidity is noted a few minutes after mixing.

SCHEME OF IDENTIFICATION

The above tests are used as follows:

I. ALKALINITY OF ASH, BELOW 0·15; *test* (*a*), blue:
  - (i) *Test* (*b*), purple.
    - (1) *Test* (*c*), turbid:—*E. crebra* (few), *dealbata, propinqua, siderophloia, sideroxylon, trachyphloia.*
    - (2) *Test* (*c*), clear:—*E. dealbata, polyanthemos, rostrata, siderophloia, tereticornis.*
  - (ii) *Test* (*b*), pink.
    - (1) *Test* (*c*), turbid:—*E. punctata, sideroxylon.*
    - (2) *Test* (*c*), clear:—*E. corymbosa, grandis, haemastoma, micrantha, punctata, rubida, saligna.*
  - (iii) *Test* (*b*), negative.
    - (1) *Test* (*c*), turbid:—*E. sideroxylon.*
    - (2) *Test* (*c*), clear:—*E. marginata, resinifera, robusta.*

II. ALKALINITY OF ASH, 0·15 TO 0·30; *test* (*a*), blue:
  - (i) *Test* (*b*), purple.
    - (1) *Test* (*c*), turbid:—*E. crebra* (few), *longifolia, propinqua* (few), *siderophloia, trachyphloia.*
    - (2) *Test* (*c*), clear:—*E. polyanthemos* (few), *siderophloia.*
  - (ii) *Test* (*b*), pink:—*E. botryoides, corymbosa, grandis, punctata* [a few samples produced a turbidity with *test* (*c*)], *rubida, saligna.*
  - (iii) *Test* (*b*), negative.
    - (1) *Test* (*c*), turbid:—*E. longifolia.*
    - (2) *Test* (*c*), clear:—*E. robusta.*

III. ALKALINITY OF ASH, 0·30 TO 1·00; *test* (*a*), blue:
  - (i) *Test* (*b*), purple.
    - (1) *Test* (*c*), turbid:—*E. accedens, bicolor, crebra, longifolia, melanophloia, redunca.*
    - (2) *Test* (*c*), clear:—*E. accedens, bancrofti, bicolor, crebra, fergusoni, paniculata, redunca, seeana.*
  - (ii) *Test* (*b*), pink:—*E. botryoides, corymbosa* (few), *rubida, saligna* (few).
  - (iii) *Test* (*b*), negative:—*E. longifolia.*

IV. ALKALINITY OF ASH, 0·30 TO 1·00; *test* (*a*), green:—*E. haematoxylon*; [*test* (*c*) always turbid], *diversicolor.*

V. ALKALINITY OF ASH, 1·0 TO 2·0:
  - (i) *Test* (*a*), blue; *test* (*b*), purple.
    - (1) *Test* (*c*), turbid:—*E. accedens* (few), *bicolor, eximia, melanophloia, microtheca, redunca.*
    - (2) *Test* (*c*), clear:—*E. accedens* (few), *bancrofti, bicolor, microtheca, paniculata, redunca, seeana.*
  - (ii) *Test* (*a*), green:—*E. salmonophloia* [*test* (*c*), clear], *diversicolor.*

VI. ALKALINITY OF ASH, OVER 2·0:
  - (i) *Test* (*a*), blue; *test* (*b*), purple:—*E. bicolor, microtheca, eximia* [*test* (*c*), turbid], *tesselaris* [*test* (*c*), turbid].
  - (ii) *Test* (*a*), green:—*E. campaspe, salubris* [*test* (*c*), clear, in both cases].

ADDITIONAL CHEMICAL TESTS.—Two ml. of extract (i) are used for tests 1 to 5.

(1) Five drops of 1 per cent. ammonia or 1 drop of 10 per cent. lithium hydroxide solution are added:—*E. longifolia* or *resinifera*, brown colour; *E. marginata* or *robusta*, straw to pink.

(2) Saturated lime water (5 drops) or baryta water (3 drops):—*E. longifolia*, green precipitate; *E. robusta* or *rostrata*, light brown or red-brown precipitate.

(3) Three drops of 3 per cent. ammonium molybdate solution:—Precipitate with *E. dealbata, longifolia, polyanthemos* and *tereticornis*, but not with *E. resinifera*.

(4) Five drops each of 1 per cent. potassium hydroxide and basic lead acetate solutions:—*E. haemastoma* or *micrantha*, red-brown precipitate; *E. rubida*, light-brown.

(5) One per cent. potassium dichromate solution (5 drops):—*E. haemastoma* or *micrantha*, turbidity; *E. rubida*, clear.

(6) To 5 ml. of extract (ii) are added 5 drops of a 1 per cent. solution of zinc acetate in alcohol:—*E. longifolia* and *rostrata*, green-yellow precipitate; *E. robusta*, different shade.

(7) To 2 ml. of extract (iii) are added 5 drops of saturated lime-water:—*E. longifolia* or *rostrata*, pink-brown precipitate; *E. robusta*, negative.

(8) To 2 ml. of extract (iii) are added 10 drops each of 1 per cent. potassium hydroxide and copper sulphate solutions:—*E. dealbata*, drab-green; *E. longifolia*, light-blue.

J. G.

International Atomic Weights

FIFTH REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY*

THE report covers the year ending September 30, 1934. The only change in the Table is from 93·3 to 92·91 for niobium. The determination of the density of propylene, prepared by two different methods, led to the value C = 12·005. The densities of oxygen, carbon monoxide, and nitrogen were determined in the same apparatus, with results of C = 12·006 and N = 14·0083. The re-determination of the density of ammonia gas gave practically the same value, *viz*. 14·008. The ratio between sodium chloride and silver was again determined, the average atomic weight for sodium working out at 22·994. Carefully purified calcium chloride prepared from various raw materials gave the following values for calcium:

Coral limestone, Bermuda:	40·077
Marine shells, Fifeshire:	40·076
Pegmatite, Portsoy, Banffshire:	40·087
Pegmatite, Rhiconich, Sutherlandshire:	40·092

The density of krypton (3·743), purified over calcium, then by fractional distillation, corresponds with an atomic weight of 83·66. The ratio of niobium pentachloride to silver gave the new figure Nb = 92·909, which agrees almost exactly with Aston's conclusion that niobium is probably a simple element with an atomic weight of 92·90 on the chemical scale. Caesium chloride, spectroscopically free from potassium and rubidium, was compared with silver by the conventional method, giving the value Cs = 132·911. Tantalum pentachloride, purified by sublimation *in vacuo*, was analysed by the same method, and the result, 180·89, agrees exactly with Aston's figure. The determination of the atomic weight of lead from the pitchblende deposit near Great Bear Lake, Canada (conversion of lead chloride into silver chloride), resulted in the value 206·054 (*cf*. ANALYST, 1934, **59**, 414).

W. R. S.

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* By G. P. Baxter, O. Hönigschmid, P. Lebeau, and R. J. Meyer (*J. Amer. Chem. Soc.*, 1935, **57**, 787).

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Pasteurised Milk. M. Schnetka. (*Z. Unters. Lebensm.*, 1935, **69**, 235–248.)—By none of the methods previously described is it possible to ascertain beyond doubt if a milk has been pasteurised by being heated for 30 minutes at 62° to 65° C. It is, however, now found that this can be done by a procedure based on the observation that the readily-coagulable portion of the lactalbumin in ammoniacal milk is precipitated by ammonium sulphate more readily than in neutral or acid milk and to an extent dependent on the temperature and duration of the heating. The procedure is as follows:—Into two test-tubes (18 × 2 cm.) are placed 20 ml. of milk, 0·2 ml. of 10 per cent. ammonia solution being added to one. To each are added 3·5 g. of finely-ground ammonium sulphate, the tubes being then shaken vigorously 40 or 50 times, and the contents filtered through hard filter-papers (Schleicher und Schüll, No. 605) in covered filters. The ammonical sample filters fairly rapidly and often gives an opalescent filtrate, but the other filters clearly and very slowly. The filtration may be left to go on during the night as the sera are highly stable. Of each of the two filtrates, 1 ml. is mixed in a small test-tube (9 × 1·2 cm.) with 4 ml. of a slightly ammoniacal 1 per cent. ammonium acetate solution (containing 1 ml. of 25 per cent. ammonia solution per 100 ml.). The tubes are placed in a boiling water-bath heated by a Bunsen flame regulated to bring the bath to boiling-point again in 1·5 minute. After the total time of immersion reaches 5 minutes, the tubes are cooled and their contents are poured into Thöni tubes (for determining lactalbumin), each division of which corresponds with 1·5 c.mm. The tubes are fitted into a cork, and the cork into the brass thimble of a centrifuge used for Gerber's fat determination. The tubes are closed and centrifuged for 15 minutes at 1550 r.p.m. The volumes of the two precipitates—S for the tube without and AS for that with ammonia—are read in divisions of the tubes immediately after the centrifuging. For milk properly pasteurised it is found that: S + AS is not greater than 24, S : AS is at least 1·4, and AS is not greater than 10. The limiting value 1·4 for the ratio S : AS would indicate either insufficient pasteurisation or admixture with raw milk. Confirmation of the insufficiency of the pasteurisation may be obtained by heating the milk for a shorter or longer time to the pasteurising temperature, and repeating the test. Addition of comparatively small proportions of raw milk to pasteurised milk are detectable in this way, and even with soured milk the efficiency of the pasteurisation may often be judged. (*Cf.* Kay and Neave, *Lancet*, 1935, **228**, 1516.)

T. H. P.

Investigation of Eggs. K. Eble and H. Pfeiffer. (*Z. Unters. Lebensm.*, 1935, **69**, 228–235.)—The colorimetric determination of phosphate in egg albumin is disturbed by the colour of the albumin and by the turbidity it imparts to the solution. This difficulty is overcome by dialysing the albumin into water quite free from silicate and phosphate at a temperature not above 18° C., and using the dialysate for the determination. At higher temperatures, hydrolytic fission of the organically-bound phosphorus appears to take place. A single dialysis only is carried out, although it does not entirely remove the crystalloids from the albumin; repeated dialyses continue to give dialysates containing phosphate, this being derived from organic phosphorus compounds.

For determining the phosphate in the dialysate, the solutions required are: (i) 20 g. of hydroquinone and 1 ml. of sulphuric acid in 1000 ml. of water. (ii) 1000 ml. of 20 per cent. sodium carbonate (anhydrous) solution and a solution of 37·5 g. of sodium sulphite in 250 ml. of water are mixed and filtered (stable only for 8 to 10 days). (iii) 25 g. of powdered ammonium molybdate are dissolved in 500 ml. of cold phosphorus-free *N* sulphuric acid. (iv) 4·394 g. of monocalcium phosphate, finely powdered and dried for some days in a desiccator over sulphuric acid, are dissolved in 1000 ml. of water, a few drops of chloroform being added as preservative; 1 ml. ≡ 1 mg. P ≡ 3·063 mg. PO_4. Ten ml. of the dialysate are treated with 5 ml. of solution (i) and 5 ml. of (iii), and, after 5 minutes, with 25 ml. of (ii). After the lapse of 10 minutes, the liquid is transferred to the colorimeter-tube and compared a few minutes later with the standards. These are made by diluting 1 to 5 ml. of (iv) to 10 ml. and treating as just described.

It is found that amounts of mineral phosphate (PO_4) up to 1·5 mg. in 100 g. of the albumin show the eggs to be not above 1 to 2 weeks old, and that the mineral phosphate which diffuses from the yolk to the albumin as the egg ages is not derived from the phosphatids of the yolk, but represents mineral phosphate present as such in the yolk. Cold-stored eggs are to be preferred in every way to eggs preserved by means of water-glass or lime. T. H. P.

Counterfeited Truffle Preserve. C. Griebel. (*Z. Unters. Lebensm.*, 1935, **69**, 251–253.)—The material described, sold as "finest black truffles," consisted mostly of approximately cubic pieces of about 1 cm. side and of unnatural black colour and peculiar taste and smell, quite unlike those of truffles. The sauce was yellowish-brown and acid, benzoic acid being present as preservative. The interior of the pieces was pale brown and from the outer black portions 96 per cent. alcohol extracted a deep violet dyestuff which dyed mordanted wool grey-violet or, in strong solution, blue-black. Few ascospores were visible and the ascus spores characteristic of truffles were entirely lacking. The species of the fungus was not determined exactly, but the size of the pieces indicated one of the large *Lactaria* species. T. H. P.

Colouring Substances of Cane Sugar, I. I. Sakuma and I. Momose. (*J. Soc. Chem. Ind., Japan*, 1935, **38**, 161–163 B.)—According to Lunden (*Cbl. Zuckerind.*, 1925, **33**, 1013; 1926, **34**, 368; 1927, **35**, 73,220) raw sugar juice contains "amethyst" colour which is detrimental, in that it is adsorbed during crystal growth and cannot be removed with activated carbon. The maximum colour-depth is at *p*H 6·0 to 7·0, and the ratio (*Q*) of the absorption at 472·0*mμ* and 590·0*mμ* is between 1·5 and 3·0. It is removed by liming, carbonation, filtration over charcoal, treatment with kieselguhr and re-boiling. The affected portions of air-dried cane bagasse which had been attacked by red rot disease (*Colletolrichum Falcatium*, Went.) were digested with acetone, and the extract was diluted with an excess of water and filtered. The solvent was removed from the filtrate by evaporation, and the precipitate formed on addition of 10 per cent. silver nitrate solution was washed and decomposed with hydrogen sulphide, the material being then concentrated and dried over sulphuric acid in a vacuum. Extinction coefficients obtained with 0·004 per cent. solutions in a König-Martens spectrophotometer are recorded for 450·0 to 700·0$m\mu$ and pH 3·0 to 11·0; Q at pH 7·0 was 1·886. Saccharetin was isolated from minced, washed bagasse by digestion with cold 3 per cent. sodium hydroxide solution for 48 hours. The filtrate from this operation was treated with Fehling's solution, which precipitated the gum, the residual liquid portion being then precipitated with sulphuric acid. A filtered solution in alcohol of this precipitate was precipitated by dilution with water, the resulting saccharetin was dried in a vacuum, and the extinction coefficients were determined on a 0·01 per cent. solution Q at pH 7·0 was 2·64. J. G.

Detection and Determination of Gluconic Acid. W. Diemair, B. Bleyer, and L. Schneider. (*Z. Unters. Lebensm.*, 1935, **69**, 212–220.)—The detection of gluconic acid as its calcium salt is attended with various difficulties, especially in fruit, where the amount of the acid is small in comparison with the total amount of extractives. Use is, therefore, made of the phenylhydrazide of the acid, by means of which 0·012 g. of the acid may be detected in its pure solution. The detection is not disturbed by the substances characteristic of fruit juices and fruit wines, *viz.* glycerol, sorbitol, tannin, malic and citric acids. When, however, dextrose is present, dextrose phenylosazone is precipitated along with the gluconic acid phenylhydrazide; the latter is more readily soluble in hot water than the osazone, and this permits of a separation, although only of a qualitative one.

To determine gluconic acid in cider, 50 ml. are evaporated under diminished pressure and in a stream of carbon dioxide until a dark brown syrup mobile when cold is obtained. After addition of 5 ml. of glacial acetic acid and 1·5 ml. of phenylhydrazine, the liquid is heated for 30 minutes on a water-bath, cooled, and stirred with 10 ml. of ethyl acetate for 3 hours, during which time it is kept cold with ice. The precipitated gluconic acid phenylhydrazide is filtered off, washed with ether, dried at 60° C., and weighed. After repeated crystallisation from water, it has the m.p. 195° C. With 0·07 to 0·09 g. of the acid, about 70 per cent. is recovered in this way. Gluconic acid cannot be detected in pure apple juice by this procedure, the reaction with phenylhydrazine being prevented by the large proportions of protein, tannin, and carbohydrate present. T. H. P.

Identification and Determination of Citral. J. Bougault and E. Gattelain. (*J. Pharm. Chim.*, 1935, **127**, 437–449.)—The presence of citral accelerates the changes of colour from blue to pink shown by alcoholic solutions of methylene blue when potassium or sodium hydroxide is added. The methylene blue used must be tetra-methylthionine hydrochloride and not the double zinc salt often sold under the name. Five ml. of an alkaline alcoholic solution of methylene blue (obtained by mixing as needed, 1 drop of a 1 per cent. alcoholic solution of methylene blue and 20 ml. of 0·1 N alcoholic sodium hydroxide solution) are placed in a test-tube, 12 cm. by 12 mm., and a methyl alcohol (98–99 per cent.) solution of citral is added, drop by drop, from a 1-ml. pipette graduated in hundredths. The liquids are then carefully mixed. The addition of 1 mg. of citral at 15° C. will cause an immediate change to pink, and 0·2 mg. will cause the blue colour to become paler. Many of the constituents of essential oils will bring about the same change, but only if present in proportions ranging from 74 mg. to 772 mg. A higher temperature will accelerate the reaction. In order to determine the proportion of citral present, it is necessary first to form an approximate estimate of the quantity by preparing solutions of pure citral in methyl alcohol (98 to 99 per cent.) containing, respectively, 1, 2, 3, 4, and 5 g. per cent. by vol. Two drops of each solution are placed respectively in 5 test-tubes, 12 cm. × 12 mm. (with a mark at 5 ml.), and in the sixth tube 2 drops of the unknown solution, and the mixtures are made up to 5 ml. with the alkaline solution of methylene blue (10 drops of a 1 per cent. solution of methyl blue mixed with 40 ml. of 0·1 *N* sodium hydroxide solution). The tubes are corked and shaken at once, and a comparison of the tint in the unknown solution with those of the other tubes at the same moment will give an approximate idea of the proportion of citral present. The determination is now repeated, but within more exact limits, and the range of strengths used for comparison will now differ from one another only by 0·1 g. Citral may thus be determined in complex mixtures and in essential oils. D. G. H.

Eucalyptol and Eucalyptus Oil. B. P. Revision. J. Hendry and P. A. Berry. (*Perf. and Essential Oil Rec.*, 1935, **26**, 117.)—*Eucalyptol.*—Since eucalyptol of 99 per cent. purity is a regular article of commerce, this strength is suggested as a minimum, and the f.p. should then be not less than +0·8° C. Assay by means of the orthocresol method is regarded as unnecessary, and in any case the method is not sufficiently accurate for cineole itself. *Eucalyptus Oil.*—It is suggested that the present range of sp.gr. is too stringent, and that the lower limit be reduced to 0·905. Oils that in other respects conform to the B.P. Standards and contain 70 or more per cent. of cineole have been found to have sp.gr. at 15·5°/15·5° from 0·909 to 0·902. An oil containing 30 per cent. of hydrocarbons with an average sp.gr. of 0·86 (and many terpenes normally found in eucalyptus oil are still lower in sp.gr.) and 70 per cent. of cineole, would have sp.gr. 0·908. Also, the introduction of a standard limiting the aldehydes and ketones calculated as $C_{10}H_{14}O$ to 1·5 per cent. results in a lowering of the sp.gr. of the oil. D. G. H.

Oils of *Artemisia rigida* (Nutt.) Gray. G. Norin and R. L. McMurray. (*Amer. J. Pharm.*, 1935, **107**, 177–178.)—The scab-land sagebrush, restricted to Eastern Washington and Oregon and adjacent districts, is a low shrub with sessile flattened leaves, with a leafy spike of yellow disc flowers. The dried and ground flowering tops were subjected to steam-distillation and yielded 0·56 per cent. of a volatile oil consisting of 27·92 per cent. of stearoptene and 72·08 per cent. oleoptene at 15° C. The oleoptene was yellowish in colour, of a camphoraceous odour, acid to litmus, and miscible with absolute and 95 per cent. alcohol, acetone, glacial acetic acid, chloroform, ether and petroleum spirit, but not with carbon disulphide. It had the following characteristics:—Sp.gr. 25°/25° C., 0·9367; α_D^{25} (100 mm. tube), −15·68°; specific rotation, 25° C., −16·75°; n_D^{25}, 1·4674; acid value, 3·63; ester value, 19·46, and saponification value, 23·09. After removal of the volatile oil, the dried material was extracted with 95 per cent. alcohol, the extract was shaken out with petroleum spirit, the air-dried material yielding 1·88 per cent. of a viscid, dark green fatty oil having the following characteristics:—Sp.gr. at 40°/40° C., 0·9945; n_D^{40}, 1·4968; saponification value, 128·3; iodine value, 58·7; acid value, 36·68; and ester value, 91·64. D. G. H.

Identification of Cinchona Preparations by the Erythroquin and Thalleioquin Reactions. R. Monnet. (*J. Pharm. Chim.*, 1935, 127, 450–456.) Cinchona preparations may be rapidly identified by the erythroquin and thalleioquin reactions, but the latter is the more sensitive test. In each case very small quantities of the cinchona preparation must be used. The sample in 10 ml. of water, is placed in a small separating funnel and rendered alkaline with 10 drops of ammonia or 5 drops of sodium hydroxide solution, and 5 ml. of chloroform are added. After shaking, the chloroform solution is filtered through cotton wool. About 4 ml. of the extract is obtained, and 2 ml. are taken for each reaction. *Erythroquin test.*—To 2 ml. of the chloroform extract are added 3 ml. of 1 per cent. acetic acid, and, after shaking, the characteristic blue fluorescence is noted. Drop by drop, are then added bromine water (1 : 10) until a yellow colour persists; a 1 in 10 solution of potassium ferrocyanide (1 drop for every 5 of bromine water); and ammonia solution (1 in 10) until the mixture is slightly alkaline. After shaking, the chloroform layer shows a pink or red colour according to the quantity of quinine present. *Thalleioquin test.*—The procedure is the same as described above, but instead of potassium ferrocyanide and before the ammonia, 1 drop of sodium hydroxide solution is added; this causes the colour to form more rapidly. If the mixture is not shaken after addition of the ammonia the green colour is seen in the supernatant layers, whilst the lower layers in contact with the chloroform are pink. Chloride-of-lime solution (1 per cent.) may be used instead of bromine water in both these reactions. The quantities of various cinchona preparations suitable for these reactions are given; for the erythroquin test from a half to a third of the quantity required for the thalleioquin test is necessary; *e.g.* red cinchona powder 2 cg.; fluid extract of red, 2 drops; tincture, 20 cg. or 10 drops; cinchona wine 3 to 5 ml.; pills of aloes and cinchona extract, ½ a pill. Substances usually found associated with cinchona do not interfere with the reactions, but with complex preparations other identification reactions may be necessary. For instance, opium preparations give a weak reddish-brown colour (due to morphine) in the thalleioquin and erythroquin reaction, but the colouring substance is not extracted by chloroform. D. G. H.

Detection of Morphine in Papaverine Hydrochloride by means of Iodic Acid. J. Rozeboom. (*Pharm. Weekblad.*, 1935, 72, 498–500.)—In the test previously described (*id.*, 1935, 72, 393) it was noted that a yellow colour was developed on addition of iodic acid to morphine in the presence of papaverine hydrochloride, and this was attributed to free iodine; it produced a violet colour when shaken with carbon disulphide or carbon tetrachloride, but not with chloroform. This difference is now attributed to the fact that papaverine hydrochloride is very soluble in chloroform, but is almost insoluble in the other two solvents. If a dilute solution of iodine in water (prepared without the addition of potassium iodide) is mixed with 50 mg. of papaverine hydrochloride and a drop of dilute sulphuric acid, a brown-red precipitate results. If 0·5 ml. of chloroform is then added and the mixture is shaken, no change occurs, whilst if either of the other solvents is used, the solvent layer turns to red-violet. Alcohol (which may be present in pharmaceutical chloroform), should be absent; it also interferes with the colour produced by carbon tetrachloride or carbon disulphide, and it is therefore advisable to pre-treat the solvent with concentrated sulphuric acid, or to use the minimum amount of solvent. Carbon disulphide is recommended for tests for morphine. J. G.

Ergobasine. A New Alkaloid of Ergot of Rye. A. Stoll and E. Burckhardt. (*Comptes rend.*, 1935, **200**, 1680–1683.)—Ergobasine may be isolated from the total alkaloids of ergot by heating the fine powder with water, and slowly extracting the aqueous solution with chloroform. After concentration and standing, the crystals of ergobasine separate and may be purified by re-crystallisation from trichloroethylene or benzene. Ergobasine may also be isolated by treating a preparation of the total alkaloids with chloroform, and, since ergobasine is only feebly soluble in chloroform (1 in 5000 in the cold, and 1 in 750 hot), it will crystallise out on concentrating the solution. The crystals approximate right-angled prisms in form, and dissolve in water (1 in 200 to 300) to form a solution alkaline to litmus, with an intense blue fluorescence. They are very soluble in methyl and ethyl alcohols and in ethyl acetate. Re-crystallised from alcohol and dried to constant weight, ergobasine has a m.p. of 159° C., and decomposes at 162° C. Its optical activity in 0·25 per cent. aqueous solution is $[\alpha]_D^{20} = +90°$, and is thus at once distinguished from Dudley's ergometrine, which is also a crystalline product, but is laevorotatory. Ergobasine, which gives positive reactions with the usual reagents for alkaloids, has the formula $C_{19}H_{23}O_2N_3$. D. G. H.

Alkaloids of Han-Fang-Chi. K. K. Chen and A. L. Chen. (*J. Biol. Chem.*, 1935, **109**, 681–685.)—The Chinese drug han-fang-chi contains an average of 2·3 per cent. of total alkaloids, one of which has been isolated in a pure form. This has four methyoxy and two methylamino groups and appears to be identical with tetrandrine $C_{38}H_{42}O_6N_2$. Several salts have also been prepared. The drug yields 3·48 per cent. of ash, which contains iron, aluminium, calcium, potassium, sodium, sulphur, and phosphorus. S. G. S.

Strophanthin of *Strophanthus Emini*. J. D. Lamb and S. Smith. (*Quart. J. Pharm.*, 1935, **8**, 71–74.)—The seeds of *Strophanthus Emini* yield E-strophanthin, which resembles in characteristics and reactions the present official K-strophanthin, although it may be distinguished from the latter by the phenol-hydrochloric acid and the resorcinol hydrochloric acid tests (Smelt, *Quart. J. Pharm.*, 1933, **6**, 467). E-strophanthin consists of a complex mixture of glycosides similar in type to, but not identical with, K-strophanthin, and its biological activity appears to be equal to that of the official product. S. G. S.

Chemical Evaluation of Plant Materials containing Rotenone (Derris Root, Tubé Root, etc.). P. A. Rowaan. (*Chem. Weekblad*, 1935, **32**, 291–295.)—Economic, entomological and chemical details concerning rotenone, $C_{23}H_{22}O_6$, are discussed. In the pure state it is a white hygroscopic solid, m.p. 163° C., [α] (benzene) −233°, very soluble in chloroform, ethylene dichloride, benzene, acetone or toluene, but only slightly soluble in ether, ethanol or carbon tetrachloride (0·6 g. in 100 ml. at 20° C.); the formation of a complex compound with carbon tetrachloride (*cf.* Jones and Smith, *J. Amer. Chem. Soc.*, **1931**, **53**, 2738) is made the basis of the determination. Various methods are discussed, but the following is preferred:—The material is ground to pass a sieve with holes 0·5 mm. in diameter, and 50 g. are digested for 6 hours with 200 ml. of cold chloroform. The mixture is stirred occasionally and is finally filtered through a 20-cm. paper into an Erlenmeyer flask, the residue being washed with 50 ml. of chloroform and then returned to the original beaker and re-digested with 100 ml. of fresh chloroform. On the next day the filtration is repeated, two 50-ml. portions of chloroform being used for washing. The extract is evaporated to dryness, the last traces of solvent being removed by heating the liquid over a naked flame in a flask through which carbon dioxide is passed. The residue is then heated for a few minutes with 20 ml. of boiling carbon tetrachloride under a reflux condenser, and the rotenone and carbon tetrachloride complex (containing about 72 per cent. of the former) separates on cooling; complete separation is ensured by seeding with a small quantity of the precipitate and placing the mixture in an ice-chest overnight. The precipitate is filtered on a glass crucible (Jena, G.3), washed with 15 ml. of carbon tetrachloride (saturated with rotenone) in small portions, and then dried in air at the temperature of the room until constant in weight, when the factor 1·44 gives the rotenone-content. Determinations of moisture and ethereal extract are made in the usual way. Normal values (percentages) for derris and Surinam tubé (*Lonchocarpus*) roots are, respectively:—Moisture, both 7 to 8; ethereal extract 15 to 20, 4 to 8; rotenone, 5 to 8, 1 to 20 (extreme values found for derris root, 0 to 13·8). J. G.

Determination of Silver in Organic Medicaments, with Particular Reference to Colloidal Silver Ointment. G. Antoine. (*J. Pharm. Chim.*, **1935**, **127**, 457–465.)—The perchloric acid technique of Kahane and his collaborators (*J. Pharm. Chim.*, **1932**, **16**, 194, etc.) for the destruction of organic substances has been applied to the determination of silver in organic compounds. From 0·1 to 0·3 g. of the dried sample is weighed into a 100-ml. flask, and 3 ml. of sulphuric acid (sp.gr. 1·84) and 5 ml. of nitric acid (sp.gr. 1·38) are added. When the fumes have ceased and the liquid is black, a mixture of 2 parts of perchloric acid (sp.gr. 1·61) and 1 part of nitric acid is added, drop by drop, until the liquid is entirely decolorised. After boiling for 1 to 2 minutes to dissolve the precipitate of silver chloride and drive off the perchloric acid, the mixture is cooled, and 20 ml. of water and 2 ml. of a saturated solution of ammonia alum are added, and the silver is titrated with 0·1 *N* potassium thiocyanate solution. With collargol the quantity of sulphuric acid taken should be augmented to 5 ml. for a 0·3 g. sample of ointment. Samples of colloidal silver ointment, which should contain 15 per cent. of colloidal silver, were found to be very deficient therein, probably owing to lack of care in the preparation, since a simple mixing of colloidal silver with lanoline would result in a higher proportion of silver being found in the ointment on the periphery of the mortar. D. G. H.

Biochemical

Measurement of the *p*H Value and Acid-Neutralising Power of Saliva. B. C. Soyenkoff and C. F. Hinck. (*J. Biol. Chem.*, 1935, **109**, 467–475.)—The MacInnes glass electrode and the capillary quinhydrone electrode were used to determine the *p*H value of saliva. The results differed by less than 0·02 *p*H unit, although the glass electrode was easier to handle. The average value obtained for resting saliva was *p*H 6·64, and for stimulated saliva 7·13. Saliva acts as a buffer solution on the alkaline side of *p*H 4·0, and resting saliva varies considerably in its acid-neutralising power. S. G. S.

The Acetonitrile Test for Thyroid. F. Wokes. (*Quart. J. Pharm.*, 1935, **8**, 54–60).—The susceptibility of mice to acetonitrile poisoning and the degree of protection afforded by the administration of thyroid are both found to be affected by the temperature at which the mice are kept. At 38° C. thyroid has practically no protective action, and the average lethal dose of acetonitrile is only about one-fifth of that at room temperature. A protective action is noticeable at lower temperatures, but, since the dose-mortality curve becomes flattened, a quantitative use of the acetonitrile test for thyroid is accompanied by many difficulties.
S. G. S.

Proteins of Meat. E. C. Bate Smith. (*J. Soc. Chem. Ind.*, 1935, **54**, 152T.)—The muscle substance proper consists of the two proteins, myosin and myogen, which belong to the globulin class of proteins. The tendons and connective tissue consist mainly of two insoluble fibrous proteins, collagen and elastin. Collagen is easily converted into gelatin by boiling or autoclaving with water, whereas elastin is not affected by this treatment. Both myosin and myogen exhibit the usual properties of the globulins, particularly with regard to the readiness with which they undergo denaturation, myogen being more easily denaturated than myosin. A third globulin, "globulin X," is probably also present. For analytical purposes it has been found that 7 per cent. lithium chloride solution is as efficient for extraction purposes as 10 per cent. ammonium chloride solution, and that exhaustive extraction with hydrochloric acid can be used instead of tryptic digestion as a means of removing the residual intercellular fraction.
S. G. S.

Post-mortem and Refrigeration Changes in Meat. T. Moran. (*J. Soc. Chem. Ind.*, 1935, **54**, 149T.)—After death, the glycogen of living tissue breaks down to lactic acid, and the phosphagen decomposes into phosphoric acid and creatine. The autolysis of the tissue and the proteolytic action of bacteria commence as soon as *rigor mortis* has passed, and other changes will include the oxidation of fat deposits, the change of haemoglobin into methaemoglobin, evaporation of water, and the denaturation of the proteins. The onset of bacterial attack will depend upon the numbers and type of bacteria initially present, and, although this action may be delayed by freezing to −7° C. or −10° C., yet quality is lost, owing to the tissue structure being broken down by the freezing. At 0° C. denaturation of the muscle protein appears to be inappreciable, although up to 40 per cent. may occur in 24 hours at 30° C. At −2° C. or −3° C., however, denaturation may take place, owing to the effect of the altered *p*H value and salt concentration in the liquid phase of the partly-frozen muscle. Fat rancidity is affected by light, and, although beef and mutton fats are relatively resistant, bacon fat is more susceptible, probably owing to the action of the salts in the pickling liquor. The use of gaseous carbon dioxide in the storage chamber requires careful adjustment, for, since the formation of methaemoglobin is influenced by the partial pressure of oxygen present, a change of this kind destroys the "bloom" of the meat.

S. G. S.

Constituents of Meat acting as Pointers of Change. L. C. Baker. (*J. Soc. Chem. Ind.*, 1935, **54**, 154T.)—From an analytical point of view, the chief indicators of incipient putrefaction are the *p*H value and the amount of ammoniacal nitrogen. If the *p*H value is above 6·2, it is presumptive evidence of deterioration; and if the ammoniacal nitrogen exceeds 0·02 to 0·025 per cent., putrefaction may be assumed to be taking place. The amount of lactic acid increases in meat after death, and appears to assist the softening of the muscle fibres. The determination of moisture, proteins and extractives are of more value in comparing cooked with uncooked meats than in determining the freshness of the latter. The colour of meat, which is closely linked with its haemoglobin-content, is a useful guide to the freshness of raw meat, and in cooked meats varies with the method of cooking. The amount of free fatty acids in fats will often indicate bacterial activity, and this will affect the flavour, for a taint may appear if the free fatty acids exceed 1·0 per cent. The determination of active oxygen is also of value, especially with bacon. S. G. S.

Proteins of Yeast (*Saccharomyces Cerevisiae*). F. A. Csonka. (*J. Biol. Chem.*, 1935, **109**, 703–715.)—Determinations of amino acids in preparations of yeast protein have been made both with bakers' and brewers' yeast. The results obtained with bakers' yeast were:—Cystine, 0·44; tryptophane, 2·66; and tyrosine, 4·79 per cent. For brewers' yeast the results were:—Cystine, 0·49; tryptophane, 2·67; tyrosine, 4·11; arginine, 3·50; histidine, 1·38; and lysine, 4·50 per cent., all results being calculated on a moisture-and ash-free basis. When yeast is hydrolysed, both cystine and histidine undergo a change. Since relatively large amounts of nutritionally essential amino acids are present in yeast proteins, the supplementing effect of these should be taken into consideration when yeast is added to experimental diets. S. G. S.

Separation of Tyrosine from Large Amounts of Cystine. F. R. Greenbaum. (*Amer. J. Pharm.*, 1935, **107**, 162–173.)—The method eventually evolved for the separation of tyrosine from large amounts of cystine depends on the precipitation of the cystine by acidifying an ammoniacal solution with hydrochloric acid, the tyrosine being, under certain conditions, insoluble in ammonia. For example, 16·25 g. of a mixture containing 14·87 g. of cystine were suspended in 244 ml. of water heated to about 75° C., the minimum amount of concentrated ammonia was added, and the solution was filtered (the ammonia-insoluble portion being tyrosine), cooled and submitted to fractional precipitation with dilute hydrochloric acid. Fraction I (10 g.) contained 100 per cent. of cystine and gave a negative Millon reaction; fraction II (2 g.) contained 47·66 per cent. of cystine and gave a strong Millon reaction. It was found that the isolation-point of a mixture of cystine and tyrosine is very much more on the acid side than has been thought, and a *p*H of 1·72 to 2·0 is necessary. In another experiment 25 g. of cystine and 25 g. of tyrosine were mixed, suspended in 900 ml. of water and 50 ml. of concentrated ammonia, and stirred for 1½ hours. On filtering, fraction I (insoluble in ammonia) amounted to 23 g. of tyrosine. To the filtrate 140 ml. of hydrochloric acid (1:1) were added, and, after standing overnight at a *p*H of 1·42, no tyrosine appeared. Then 68 ml. of ammonia (1:2) brought the *p*H to 1·92, and, on filtering, fraction II gave 23·5 g. or 94 per cent. of recovered cystine of 100 per cent. purity, whilst fraction III, which was obtained after standing overnight, consisted of 2·5 g. of tyrosine, thus making a 100 per cent. recovery of tyrosine. The method fails with very small amounts of cystine and very large amounts of tyrosine. D. G. H.

Vitamin *A* Content of Sweet Potato. F. L. MacLeod, M. R. Armstrong, M. E. Heap, and L. A. Tolbert. (*J. Agric. Res.*, 1935, **50**, 181–187.)—The vitamin *A* content of five varieties of sweet potato—Nancy Hall, Porto Rico, Yellow Jersey, Triumph and Southern Queen—were determined biologically by the use of the technique of Sherman and Burtis (*J. Biol. Chem.*, 1928, **78**, 671–680). The Porto Rico and Yellow Jersey varieties were examined directly on harvesting and again two months later. In both of these varieties the vitamin *A* content increases on storage, the Porto Rico rising from 20 units (Sherman) per g. to 65 units per g., and the Yellow Jersey from 10 units per g. to 40 units per g. The other varieties were examined only after being stored for some time. The Nancy Hall variety contained 30 units of vitamin *A* per g., the Triumph, 2 units per g., and the Southern Queen, 4 units per g. The Porto Rico, Yellow Jersey, and Nancy Hall varieties are strongly pigmented, Porto Rico having the deepest colour. The vitamin *A* content varies, therefore, with the depth of colour. S. G. S.

Sensitive Spot Reaction for Ascorbic Acid (Vitamin *C*). H. Tauber. (*Mikrochem.*, 1935, **17**, 111–112.)—The reagents required are: (i) 8 per cent. acetic acid solution. (ii) One g. of anhydrous ferric sulphate is boiled with 80 ml. of water and 18 ml. of 85 per cent. phosphoric acid, 1 per cent. potassium permanganate solution being added dropwise (0·6 to 0·7 ml. in all) to give a faint pink liquid. The solution is boiled for a few minutes, filtered, cooled, and made up to 100 ml. (iii) 0·4 per cent. potassium ferricyanide solution, free from ferrocyanide. No trace of blue colour should appear when equal volumes of the three reagents are mixed.

To detect ascorbic acid in plant tissue or organs, a few grams are macerated with a two- or three-fold quantity of hot 8 per cent. acetic acid solution for a few minutes in a test-tube by means of a glass rod with sharp edges. A drop of the extract is then placed on a double filter-paper, and the spot on the lower paper is treated with a drop of solution (iii), followed by one of (ii). In presence of 0·003 mg. of ascorbic acid in 0·05 ml. of the solution, a blue colour appears within half a minute; with more than 0·005 mg. of the acid, the colour shows immediately after addition of the ferric sulphate. Lemon juice contains 0·6 mg. of ascorbic acid per ml., and, when diluted threefold and tested as above, immediately gives a blue colour. If, as rarely occurs, no colour appears with one minute, absence of ascorbic acid from the juice must be concluded; after a longer time, certain tannins reduce the ferricyanide and thus show the blue reaction.

Uric acid does not disturb the test, and sugar solutions affect it only if first boiled with alkali. Large proportions of cysteine, glutathione, or pyrogallol interfere, but the amounts commonly present in tissues are without effect.

T. H. P.

New Method for the Separation of Sterols from Vitamin *D*-containing Materials. S. Natelson and A. E. Sohel. (*J. Biol. Chem.*, 1935, **109**, 687–694.) —Sterols may be separated from vitamin *D*-containing material, such as cod-liver oil, irradiated cholesterol and irradiated ergosterol, by converting them into potassium salts of their sulphuric esters. For each g. of sterol (dissolved or suspended in 5 ml. of chloroform) 0·4 ml. of chlorosulphonic acid is added to 3 ml. of pyridine dissolved in 5 ml. of chloroform. Pyridine chlorosulphonate crystals separate out, but this does not affect the reaction. To this salt suspension in chloroform and excess of pyridine is added the solution of the sterol. The mixture is allowed to stand for a few minutes with occasional shaking, and then gently heated for 2 hours beneath a reflux condenser. The pyridine and chloroform are evaporated off *in vacuo,* 1 g. of potassium hydroxide (dissolved in 10 ml. of water) is added, and the mixture is cooled in ice. Vigorous shaking is necessary to effect complete transference from the pyridine to the potassium salt. The salt may be separated on a Buchner funnel and washed with water, alcohol, and then ether. If large amounts are being handled, a centrifuge may be used. The residue is then extracted in a continuous extractor with anhydrous ether, dried and weighed. The combined extracts are evaporated *in vacuo* at 35° C. to remove the alcohol and ether. The residue is extracted several times with petroleum spirit, and the extract is washed with water, dried over anhydrous sodium sulphate and evaporated *in vacuo.* Dry potassium ergosterol sulphate cannot be activated antirachitically except after boiling in aqueous solution. Insoluble potassium sulphate derivatives may be isolated from phenol, ergosterol, chlolesterol, and borneol, but not from vitamin *D* in cod-liver oil, calciferol, irradiated ergosterol, or irradiated cholesterol.

S. G. S.

Agricultural

Comparative Estimations of Phosphorus and Potassium in an Arable Soil by Hilgard's Chemical Method, Neubauer's Biological Method, and Niklas' Method with *Sterigmatocystis nigra.* A. and R. Sartory, J. Meyer and F. Arnold. (*Compt. rend.*, 1935, **200**, 1797–1799.)—The results recorded show that a weak crop of *Sterigmatocystis nigra*—in the soil extract obtained with Raulin's acid solution—after 5 days indicates insufficiency of phosphorus and potassium in the soil. A high weight of mycelia appears to show, however, that the two nutrients exist in the soil in satisfactory amounts and in the physiological equilibrium required for their perfect assimilation by vegetable organisms. The weights of the crop of the mould are sensibly proportional to the amounts of soil used. The crop is influenced more by the phosphorus than by the potassium. As indicated by Niklas and his co-workers, 2·5 g. of the soil should be taken per 30 ml. of nutrient medium. The Niklas method shows the amounts of phosphorus and potassium compounds readily soluble and readily absorbable by plants, whereas Neubauer's method takes account of all the nutritive salts of the soil available over a long period. T. H. P.

Histological Characteristics of Plants Grown in Toxic Concentrations of Boron. I. E. Webber. (*J. Agric. Res.*, 1935, **50**, 189–194.)—The irrigation waters in certain districts of the Western United States are rich in boron, and, although different species of plants tolerate different maximum and minimum proportions of boron, the excess of boron in this district becomes a factor of agricultural importance. The macroscopic appearance of boron injuries are well known, and the histological characteristics of boron-injured lemon, grape, prune and apricot leaves, and of prune, peach and apricot stems has now been studied. Leaves showed necrotic brown areas sometimes accompanied by hypertrophied and hyperplastic areas, and fewer calcium oxalate crystals were present than in normal leaves. The greatest injury in stems was in shoots, which do not live beyond the first year, although enlarged nodes may be present on branches two or three years old. Necrotic areas occur in the epidermis and parenchyma, and small cavities filled with gum are frequently present. The greatest injury is associated with the highest boron concentration. A toxic concentration of boron cannot be said to give rise to a specific reaction, but the observed abnormalities are to be regarded as correlated to the capacity of the species to respond to stimuli. It seems probable that an excessive concentration of boron in the cell often injures the protoplast to such an extent that it undergoes progressive degeneration. Under some conditions an excess of boron may stimulate the protoplast to abnormal growth or division. D. G. H.

Organic

Liver Oil of the Basking Shark. M. Tsujimoto. (*Bull. Chem. Soc. Japan*, 1934, **10**, 14–148.)—The basking shark (*Cetorhinus maximus*, Gunner) may reach 36 ft. in length. An examination of the liver-oil of (i) a female (1 month after death) and (ii) a male (a few days after death) was made. In each case the livers yielded about 79 per cent. of an orange-yellow oil which gave hardly any blue colour in the antimony chloride test. On analysis, the following figures were obtained:—Sp.gr. 15°/4° C., (i) 0·8973, (ii) 0·8808; n_D^{20}, (i) 1·4794, (ii) 1·4785; saponification value, (i) 126·3, (ii) 94·8; iodine value (Wijs), (i) 185·6, (ii) 191·5; acid value, (i) 0·16, (ii) 0·21; unsaponifiable matter, (i) 30·35, (ii) 45·13 per cent. The difference in values are chiefly due to the higher proportion of squalene in the oil of the male. The fatty acids showed: M.p., (i) 24° to 25° C., clear at 27° C.; (ii) clear at 20° to 21° C.; neutralisation value, (i) 186·4, (ii) 179·3; iodine value, (i) 130·0, (ii) 88·2; n_D^{25}, (ii) 1·4605; ether-insoluble bromide, per cent., (i) 27·0, (ii) 9·3; bromine-content of bromide, per cent., (i) 70·23, (ii) 69·63. The unsaponifiable matter, which was a pale yellow liquid (with a little solid deposit in the case of No. 1 oil), had: n_D^{20}, (i) 1·4900, (ii) 1·4863; iodine value, (i) 338·9, 302·4; cholesterol, per cent. (digitonin method), (i) 1·83, (ii) 0·94. A higher proportion of pristane was present in No. (ii) (about 6 per cent.), and it is suggested that the liver of the basking shark would be a valuable source for the preparation of pristane, as a high proportion appears to be of rather frequent occurrence. In addition to squalene and pristane, a new hydrocarbon was also found.

D. G. H.

New Hydrocarbon in Liver Oil of the Basking Shark. M. Tsujimoto. (*Bull. Chem. Soc. Japan*, 1935, **10**, 149–153.)—The pristane fraction isolated from the basking shark oils (preceding abstract) was invariably found to have an appreciable iodine value, even after purification, and, although the various methods tried for the separation of saturated from unsaturated hydrocarbons were not altogether successful, yet it was confirmed that an unsaturated hydrocarbon (or hydrocarbons) is present in the pristane part of basking shark-liver oil. The liver oil was distilled under 3 to 5 mm. pressure (with a maximum temperature of 270° C. in the bath), and the distillate was re-distilled under 9 to 10 mm. pressure. The resulting distillate was again distilled under a pressure of 10·5 to 11 mm. over metallic sodium (with a maximum bath-temperature of 215° C.). The refined distillate was subjected to the bromine-esterification method (Grün, *Analyse der Fette und Wachse*, Vol I, p. 223), and finally a residue free from halogen and squalene was obtained; it was recognised as a mixture of an octadecylene, $C_{18}H_{36}$, and pristane, the former predominating. A partly successful attempt was made to concentrate the unsaturated hydrocarbon by means of methanol, but the material was insufficient. The octadecylene, for which the name "Zamene" is proposed, is present in basking shark-liver oil in smaller proportion than was anticipated, but probably occurs in many other squalene-containing shark-liver oils, in association with pristane. D. G. H.

Determination of True Complex Sulphonic Acids in Materials used in the Textile and Tanning Industries. K. Lindner. (*Chem.-Ztg.*, 1935, **59**, 388–389.)—With the technical pure sulphonic acids or their aqueous solutions, 1 to 2 g. are dried to constant weight in a vacuum over phosphorus pentoxide and soda-lime; any small amount of sulphuric acid present as impurity is included in the weight found. If the sulphonic acid is present as salt, or if sulphuric acid is to be eliminated, the preparation is dissolved in water, neutralised with sodium hydroxide and treated dropwise with dilute hydrochloric acid until acid to Congo red. The solution is evaporated on a water-bath to expel the hydrochloric acid, and the residue is digested 3 to 5 times with 96 per cent. alcohol until the inorganic salts present are quite colourless. The total alcoholic extracts, filtered, if necessary, are evaporated on a water-bath, and the residue is digested with hot absolute alcohol to remove the last traces of salts. When cold, the liquid is filtered through a weighed porcelain crucible, the filtrate being evaporated at 85° C. and dried, finally in a vacuum over phosphorus pentoxide and soda-lime until of constant weight. If alkali salts of volatile or weak acids are present, this residue may be erroneously high. In this case the dried sulphonic acid is ashed, and the ash is converted into sulphate. The nature of the alkali is then ascertained and a correction applied to the weight found for the sulphonic acid. If the material contains a volatile solvent, this is distilled from the acidified (with hydrochloric acid) substance, the residue being neutralised, made acid to Congo red, and treated as described above.

In the textile industries, mixtures of sulphonic acid with soap or sulphuric esters of fats (red oil) are much used. If soap is present, 5 to 20 g. are dissolved in water in a separating funnel and the solution is shaken with dilute hydrochloric acid and ether to extract the fat. When sulphuric esters of fats are present, the substance is dissolved in 25 ml. of water and boiled for an hour, in a reflux apparatus with ground joint, with 50 ml. of concentrated hydrochloric acid (sp.gr. 1·19) to separate the fat. The fat is then extracted with three quantities of ether in a separating funnel. If a volatile solvent also is present, steam-distillation is carried out in conjunction with separation of the fatty acids. The united ethereal extracts are washed with water until neutral to methyl orange, the fatty acids being then determined. The aqueous solutions are warmed to expel traces of ether, neutralised. made acid to Congo red with hydrochloric acid and evaporated, the sulphonic acids being then separated as described above. If mixtures of sulphonic acids with sulphonates of aliphatic alcohols are treated as above, the mixture of aliphatic alcohol and sulphonic acid often gives a mixture difficult to separate when shaken with ether. In this case the procedure is modified somewhat and petroleum spirit is used for the extraction. The identification of the sulphonic acids is briefly discussed. T. H. P.

Acetone Method for the Determination of Sulphuric Acid and Buffer Salts in Vegetable-tanned Leather. R. F. Innes. (*J. Inter. Soc. Leather Trades' Chem.*, 1935, **19**, 183–185.)—The author's method (Abst., ANALYST, 1934, **59**, 771) was found to give negative results for the presence of sulphuric acid in old leather bookbindings which had become decayed by exposure to a polluted atmosphere for several years, and had gradually absorbed up to about 5 per cent. of this acid. This appears to be due to the formation of compounds which ionise in water, but not in 90 per cent. acetone, by combination between the sulphuric acid and the basic substances produced in the later stages of degradation of the proteins. The negative results were reproduced with solutions of degradation products of proteins containing 0·02 per cent. of nitrogen, and brought to *p*H 2 with sulphuric acid. Results obtained by various methods of analysis when the sulphuric acid is present in the leather in the combined and un-ionisable state, in the combined and ionisable state, and in the uncombined state, respectively, were:—Gravimetric, +, +, +; Procter–Searle —, +, +; Atkin–Thompson or Innes (physical), —, +, +; acetone, —, —, +. Tests on many trade samples of new leathers by the acetone method have shown the absence of mineral acids, and in some cases the absence also of buffer salts; leathers of the latter type are likely to deteriorate in a few years in a polluted atmosphere. (*Cf.* following abstract.) J. G.

Measurement of the "Acidity" of Vegetable-tanned Leather by the Acetone Method. W. R. Atkin. (*J. Soc. Leather Trades' Chem.*, 1935, **19**, 186–190.)—The erroneous results recorded by Innes (cf. *id.*, 1931, **15**, 8, and preceding abstract) have been confirmed by experiments with two rotted leathers of known history. In addition, it is stated that the method is not capable of measuring the buffer-salt content accurately, even under favourable conditions. Low results, as compared with those given by the Procter–Searle, alkalinity of ash, and electrometric titration methods are obtained in the presence of sodium formate; the presence of magnesium sulphate or acid sodium oxalate also leads to erroneous results. It is concluded that the only reliable method of ascertaining the quantity of protective salt present is titration to *p*H 3·0, preferably by means of the glass electrode. J. G.

Determination of Damage in Silk. S. R. Trotman and H. S. Bell. (*J. Soc. Chem. Ind.*, 1935, **54**, 141–142T.)—A weighed sample of the silk is placed in a small stoppered bottle, and a cold solution (sp.gr. 1·677) of zinc chloride (previously filtered through glass-wool) is added, the silk being wetted with the liquid by means of a glass rod. The mixture is incubated in the closed bottle at 37° C. for exactly 6 hours, the bottle is then cooled to 20° C., and the viscosity of the solution (2·5 per cent. w/v, sp.gr. 1·666) is determined at 20° C. in an Archbutt–Deeley viscometer provided with a 20-ml. pipette. The viscosity of the zinc chloride solution alone was always 1·425 (9·5 centipoises) compared with water at 20° C. The data given for various crude and degummed silks demonstrate the fall in viscosity with increase in time and temperature; this is due to depolymerisation of protein complexes, not to hydrolysis; no peptones or amino acids could be separated by dialysis of the zinc chloride solutions, and a lithium bromide solution of silk showed no increase in acidity (as determined by the formaldehyde method) in 7 days. Other data show that degumming decreases the viscosity, and that Japanese silk gives higher values than Italian or Chinese silks of standard quality before degumming, whilst Italian silk heads the list after degumming; the differences are not sufficient for purposes of identification. Hydrogen peroxide produces a reduction in viscosity which is considerable after 6 hours in contact with the 5-vol. reagent, or in the presence of a copper, iron or manganese catalyst. The damaging effects of 0·1 *N* hydrochloric acid or sodium hydroxide solution, and of 10 per cent. solutions of sodium chloride or sodium sulphate are also demonstrated, but mechanical damage does not produce a very material reduction in viscosity unless it is severe (*e.g.* small pieces of degummed silk after being ground with silver sand in a mortar had a value of 17·5 instead of 19 to 20 centipoises). It is concluded that the value for undamaged degummed silk should not be less than 19·0, and that a viscosity exceeding 21·0 indicates incomplete degumming (*cf.* Clibbens and Geake, *J. Text. Inst.*, 1928, **19**, 77T.). J. G.

Estimating Dyestuff Intermediates by Coupling. S. Ueno and H. Sekiguchi. (*J. Soc. Chem. Ind., Japan*, 1935, **38**, 142–144B.)—The procedure is titration of the sample with an appropriate diazo-compound which should be stable at 0° C. for several hours; it should also couple rapidly, so as to give a sharp end-point without the formation of a disazo-dye, and it should not produce an antidiazotate. The titration value should be about 26 ml. of 0·1 *N* diazo solution, of which 25 ml. are added at once from a transfer-pipette cooled in crushed ice, and the remainder from a 1 ml. pipette graduated in 0·01 ml. The indicator for the end-point is a drop of a 10 per cent. solution of H-acid in 2 *N* sodium carbonate solution spotted on a filter paper; a drop of the coupling solution is quickly placed next to it (the dyestuff being salted out beforehand), and the end-point is indicated by the appearance of a coloured line 2 minutes later at the junction of the drops, the sensitiveness being 0·03 ml. The diazo-solution is stored in crushed ice, and is prepared by adding the calculated amount of 3 *N* sodium nitrite solution to 0·025 g.-mol. of the hydrochloride, 0·0375 g.-mol. of hydrochloric acid and 5 g. of potassium bromide (as catalyst) and diluting to 250 ml.; with diazo *p*-toluidine the rate of decomposition is 0·017 per cent. per hour within the first 7 hours, whilst diazo-*p*-chloroaniline is even more stable. *m*-Phenylenediamine and *m*-tolylenediamine are determined by titration of 50 ml. of the hydrochloride, in the presence of 10 ml. of 2 *N* sodium acetate solution near 0° C. with diazo-*p*-chloroaniline, and the end-point is reached when no orange line appears at the junction of spots of the two solutions (cf. *supra*); the mean results obtained were 0·3 per cent. high with the former and 0·25 per cent. low with the latter. *β*-Naphthol is titrated in the presence of sodium hydroxide and sodium carbonate with diazo-*p*-chloroaniline, the end-point being given by H-acid (cf. *supra*), or if the excess of diazo-compound present is small, by back-titration with a 0·01 *N* solution of sodium-*β*-naphtholate (mean error —0·033 per cent.). A similar procedure is used for the naphtholsulphonic acids; the potassium salt of Schäffer's acid and the disodium salt of 1-naphthol-4.8-disulphonic acid gave satisfactory results, but the values for 1-naphthol-5-sulphonic acid were high. This procedure is also followed for the titration of amino naphtholsulphonic acids, but as diazo-*p*-chloroaniline gives high results (probably because of the formation of a disazo-dye) diazo-*p*-toluidine is used; J-acid gave satisfactory results. H-acid (0·01 g.-mol.) should be dissolved in 450 ml. of ice-water with 2·8 g. of sodium carbonate, 0·5 *N* sodium nitrite solution being then added until an excess of about 1 ml. is present. The solution is then vigorously stirred, and 40 ml. of concentrated hydrochloric acid are added all at once, the temperature being kept at 0° C. for 5 minutes, after which the excess of nitrite is back-titrated with a 0·1 *N* solution of sodium sulphanilate. J. G.

Verification of Specifications for Asphalt. D. M. Wilson. (*Contract Jour. Supplement*, 1st May, 1935.)—The necessity for verification of specifications arises from the fact that "natural asphalt rock asphalt mastic" may be adulterated with limestone, with a resulting increase in the rate of deterioration. Moreover, the sources of Seyssel rock, which gives excellent results when the bitumen-content is high, are believed to be approaching exhaustion, and only limited supplies of rock containing 5 to 6 per cent. of bitumen are now available in this country. It is generally considered that a natural asphalt rock should contain at least 8 per cent. of bitumen, and that, unless the bitumen is blended with the rock under natural conditions, the product is less effective, particularly as the process of enrichment may harden the bitumen. If the bitumen is removed from the mineral matter in a suitable solvent, St. Jean rock appears of a pale sandy colour in ultraviolet light, Sicilian and Val de Travers rocks are darker in colour, and crystalline limestone is dark brown, 20 per cent. being detectable in the presence of the other rocks. Seyssel rock appears light red-brown and crystalline limestone bright crimson, if observed under the microscope in light from a carbon-arc, which should be filtered through a piece of "uviol" glass and concentrated by means of a metallic mirror. If the de-bitumenised rock is extracted with dilute hydrochloric acid, the residues may be separated by flotation in bromoform; further separation is obtained by means of the electro-magnet, and the minerals can then be identified by optical tests under a petrological microscope. Fluorite, which is one of the heavy minerals (sp.gr. 3·18), and is sometimes mauve in colour, is always absent from commercial asphalt rocks, but many limestones, especially the carboniferous types, contain it in abundance. Useful information can also be obtained from the study of grains of the washed mineral aggregates (which frequently contain fossils) retained in an 80-mesh B.S.I. sieve. The bitumen-carrying capacity is also a useful test, because various amounts of bitumen have to be added to different rocks in order to obtain the same hardness-number (say 35); St. Jean rock mastic has a final bitumen-content of 18·5; Seyssel (Chezery). 15·0; and Matlock crystalline limestone, 12·5 (cf. *Chem. and Ind.*, 1932, **51**, 61). Good-quality mastics from genuine asphalt rocks have a high percentage of fine material passing a 200-mesh sieve; the reverse applies to limestone aggregates. The Lovibond Tintometer may be used to distinguish the bitumens recovered from various rocks (cf. *id.*, 1934, **53**, 924), as most of the bitumens used for enrichment are dark in colour, an exception being fluxed Trinidad Epure. J. G.

Inorganic

Quinaldinic Acid as an Analytical Reagent. P. Rây and A. K. Majundar (*Z. anal. Chem.*, 1935, **100**, 324–327.)—It has been shown (ANALYST, 1934, **59**, 199) that the reagent can be used for the determination of copper. The authors find that it can be applied to the determination of zinc in presence of ferric iron, aluminium, beryllium, uranium, and titanium, but not chromium, which causes low results. The iron in the solution is oxidised, if necessary, with a little nitric acid. The cooled liquid is treated with 4 to 5 g. of Rochelle salt and a little ammonium chloride, and neutralised with dilute ammonia towards mixed methyl red and methylene blue. One drop of 2 *N* ammonia and water to 150 ml. are added. The solution is heated to 50° C., and treated, drop by drop, with a solution of ammonium quinaldinate during constant stirring. A slight excess of the reagent is required. The precipitate is allowed to settle, collected in a Gooch crucible, washed with hot water (first by decantation), dried at 125° C., and weighed. The zinc factor of $Zn(C_{10}H_6NO_2)_2.H_2O$ is 0·1529. W. R. S.

Abstractor's Note.—The fate of nickel, cobalt, or manganese in the zinc determination is not mentioned.

Determination of Lead and Mercury with Anthranilic Acid. H. Funk and F. Römer. (*Z. anal. Chem.*, 1935, **101**, 85–88.)—The determination follows the lines of that of zinc, cadmium (ANALYST, 1933, **58**, 241), copper, nickel, cobalt (*id.*, 567), and manganese (*id.*, 1934, **59**, 435). W. R. S.

Volumetric Determination of Mercuric Chloride by Means of Lead Sulphide. N. A. Tananaeff and W. D. Ponomarjeff. (*Z. anal. Chem.*, 1935, **101**, 185–188.)—The reaction $HgCl_2 + PbS = HgS + PbCl_2$ is applied as follows:—The mercury solution (25 ml., approximately 0·1 *N*) is boiled with an equal volume of a suspension of lead sulphide for 15 minutes. The precipitate is filtered off and washed with hot water. The filtrate (less than 100 ml.) is heated just to boiling and titrated with 0·1 *N* sodium carbonate solution (phenolphthalein as indicator) to a pink tinge. The solution is again boiled, and, if the colour disappears, a few more drops of the alkali will complete the titration. A blank assay is required for the determination of the amount of soda which will produce the same end-point. The lead sulphide suspension is prepared from 0·5 *N* lead acetate solution slightly acidified with hydrochloric acid. The boiling-hot solution is saturated with hydrogen sulphide, and the precipitate is collected and washed quite free from hydrogen sulphide. The washed precipitate is rinsed back, an equal volume of water is added, and the suspension is stored in a glass-stoppered bottle.

W. R. S.

Determination of Small Amounts of Lead in Copper. B. Park and E. J. Lewis. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 182–183.)—Various methods for precipitating traces of lead from a copper solution were tried. The following was the most satisfactory:—A 50-g. sample of copper was dissolved in 200 ml. of concentrated nitric acid. After removal of the brown fumes by heating, 1200 ml. of water, 350 ml. of concentrated ammonia, 2 ml. of disodium phosphate solution (50 per cent.) and 50 ml. of ammonium carbonate solution were added, followed by 25 ml. of calcium chloride solution (20 per cent.) added all at once, with stirring. The precipitate was filtered off, after standing overnight, on a No. 4 Jena glass crucible; the filtrate was reserved, and the precipitate was dissolved in 25 ml. of hydrochloric acid. This solution was neutralised with ammonia, then rendered just acid, and saturated with hydrogen sulphide. The sulphide precipitate was filtered off and dissolved in nitric acid, giving a solution which contained all the lead; a second phosphate precipitation, carried out with the reserved filtrate (above), was free from lead. The lead was finally determined spectroscopically, by comparison with standard solutions of lead, according to the method of Nitchie (*Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 1). The sensitiveness of the spectroscopic method was 6×10^{-7} g. The lead-content of refined copper from various sources, determined by the above method, ranged from 0·0005 to 0·006 per cent.

S. G. C.

Determination of Copper in Copper-Molybdenum Steel. H. A. Kar. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 193.)—The mixed copper and molybdenum sulphides, obtained as in the determination of copper in ordinary steel by the hydrogen sulphide precipitation method, are ignited at a dull-red heat in a silica crucible. The residue is dissolved in hydrochloric acid. To the solution, contained in a 400-ml. beaker, are added 2 or 3 drops of nitric acid, followed by an excess of ammonia. The liquid is heated to boiling, filtered, and the precipitate is washed with ammonia water and rejected. The filtrate is diluted to 250 ml., heated to boiling, and 10 to 15 ml. of a 2 per cent. alcoholic solution of α-benzoin oxime are added to precipitate the copper, the molybdenum remaining in solution. Boiling is maintained for 1 minute, some ashless paper pulp is added to collect the precipitate, and the liquid is filtered through a paper filter; the filter is washed with hot 3 per cent. ammonia water and burnt off, and the residue is ignited to copper oxide. The method was checked by using it to determine the copper-content of some 10 molybdenum and non-molybdenum standard steels of the U.S. Bureau of Standards. The results were in satisfactory agreement with, but on the whole slightly higher than, the average certificate values. S. G. C.

Detection of Arsenic in Presence of Antimony. N. A. Tananaeff and W. D. Ponomarjeff. (*Z. anal. Chem.*, 1935, **101**, 183–185.)—Tin reduces arsenic compounds in acid solution to the hydride, those of antimony to metal. The solution to be tested is warmed with pressed tin foil and hydrochloric acid in a small flask or test-tube closed with a perforated stopper fitted with a bent glass tube. The latter contains small strips of filter paper impregnated with mercuric chloride solution. If arsenic is present, the indicator paper will show the familiar yellow to brown colour. The test can be used for an approximate colorimetric determination of arsenic. W. R. S.

Separation of Iron from Cobalt. P. Spacu. (*Comptes rend.*, 1935, **200**, 1595–1597.)—The hot, neutral or feebly acid solution (50 to 80 ml.) of ferric and cobaltous salt is treated with pyridine, drop by drop, until the precipitate flocculates, leaving the liquid clear. After addition of another 3 to 4 drops of pyridine the precipitate is collected, washed with hot water, dried, and ignited. A second precipitation may be made as a check. In the filtrate the cobalt can be determined as the complex thiocyanate $[\mathrm{Co}Py_4](\mathrm{CSN})_2$ (ANALYST, 1927, **52**, 430).
W. R. S.

Dichloro-fluorescein as Adsorption Indicator for the Volumetric Determination of Halides. K. Bambach and T. H. Rider. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 165–166.)—Eight drops of dichlorofluorescein solution (0·1 per cent. in 70 per cent. alcohol) were added to about 80 ml. of the halide solution, which was titrated with 0·05 *N* silver nitrate solution, the end-point being marked by a distinct pink colour formed in the precipitate. Good results were obtained with various inorganic chlorides, bromides and iodides in aqueous or alcoholic solution, and with a number of hydrochlorides of organic bases dissolved in 75 per cent alcohol. S. G. C.

Determination of Ozone. A. Maché. (*Compt. rend.*, 1935, **200**, 1760–1762.)—In the iodimetric determination of ozone the action of ozone on potassium iodide, giving rise to iodine and tetrathionate, is accompanied, in an acid medium, by a secondary reaction, in which iodic acid or hydrogen peroxide may be formed. Juliard and Silberschatz (*Bull. Soc. Chim. belg.*, 1928, **37**, 205) suggested the use of a neutral medium and the addition of an acceptor of hydroxyl ions consisting of a buffer solution of *p*H about 7. It is now found that, for sufficiently high concentrations of ozone (*e.g.* 40 mg. per l.), this procedure gives accurate results, provided that buffer mixtures based on potassium hydrogen phthalate are not used. For low concentrations of ozone the fluorescein method (*cf.* Benoist, Abst., ANALYST, 1919, 44, 183) gives good results, but it is essential that the *p*H value be rigidly fixed. Under these conditions the variations observed in the fluorescence are rigorously proportional to the amounts of ozone acting on the fluorescein.

T. H. P.

Microchemical

Volumetric Micro-Determination of Chloride and Potassium. B. Bullock and P. L. Kirk. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 178–180.)—*Chloride.*—To the approximately neutral chloride solution (1 ml.), contained in the cut-off end of a test-tube, were added 1 ml. of acetone and 2 drops of dichlorofluorescein solution (0·01 per cent.), and the solution was titrated with 0·005 *N* silver nitrate solution, the colour change of the adsorption indicator marking the end-point. The titration was best performed in a partially darkened room, against a white background, by the light of a "daylight" lamp placed at the side of the operator. An indication of the correct *p*H value for the titration was provided by the dichlorofluorescein colour appearing fluorescent and greenish prior to titrating, and the *p*H value of the solution was adjusted, if necessary, by the addition of acid or alkali. The addition of acetone was required to produce a sharp end-point change, and for this purpose alcohol was less satisfactory than acetone, the amount of which was not critical. Good results were obtained in tests in which 1 to 2 ml. of 0·01 *N* potassium chloride solution was taken. Chloride, bromide and iodide may be similarly titrated when "in combination with cations of all valences and types." Considerable amounts of phosphate interfered by obscuring the end-point.

Potassium.—The following method, which was used for pure solutions and also sea-water, depends on separating the potassium as chloroplatinate, which is subsequently dissolved, and the chloride ion titrated after precipitation of the platinum in neutral solution by means of magnesium. To the solution (1 to 2 ml.) contained in a 10-ml. porcelain crucible, was added an excess of chloroplatinic acid solution, and the liquid was evaporated to dryness. The residue was washed first with two successive 1-ml. portions of Solution I (80 per cent. alcohol saturated with potassium chloroplatinate), then 2 or 3 times with 1-ml. portions of 20 per cent. ammonium chloride solution (which had been shaken with potassium chloroplatinate), and subsequently, 3 or 4 times with Solution I. In the washing process the washings were sucked off through a filter-stick of sintered glass coated with a layer of asbestos. The precipitate and asbestos on the filter-stick was finally washed back into the crucible with 1 to 2 ml. of hot water. A small quantity of magnesium powder was added and the liquid was evaporated to dryness. Three ml. of water were added to dissolve the chlorides and the solution was filtered through a small paper filter. The chloride in a 1-ml. aliquot part of the filtrate was titrated as described above. Three atomic proportions of chlorine are equivalent to one of potassium. In test-experiments the maximum error was —0·006 mg. on 0·384 mg.

S. G. C.

Physical Methods, Apparatus, etc.

Fire-Proof Treatment of Wood. I. Apparatus for Determining the Ignition-point of Wood. S. Uchida, S. Ai and J. Nagasawa. (*J. Soc. Chem. Ind., Japan*, **1935**, **38**, 166–167B.)—The sample is placed in an oven, which consists of a vertical quartz tube surrounded by a coil of nichrome or platinum heating-wire and asbestos insulation, and the temperature is raised gradually. At an appropriate temperature a spark is passed from time to time between two electrodes in the quartz tube close to the sample, and the ignition-point of the gases is observed through a window in the oven; at this point the temperature is read by means of a thermo-couple inside the quartz tube, which is connected with a millivoltmeter outside. When the gas ignites, combustion continues until all the sample has burned away. Reproducible results are obtainable. J. G.

Reviews

ORIGINS AND DEVELOPMENT OF APPLIED CHEMISTRY. By J. R. PARTINGTON, M.B.E., D.Sc. Pp. x + 597. London: Longmans, Green & Co., Ltd. 45s. net.

This is a monumental work, consisting of approximately 600 pages with about 7000 numbered footnote references, each usually containing more than one citation, so that the number of single references probably exceeds 25,000, and the reader cannot fail to have a feeling of profound admiration for the author's industry and application in having obtained, read and digested such a vast amount of material.

The book treats of the materials and industries of the ancient world, or rather of seven of the earliest and most important civilisations of that world, namely, those of Egypt; Babylonia and Assyria; the Aegean (Crete, Malta, Troy, the Cyclades, Mycenae, Tiryns and Cyprus); Asia Minor (Hittites, Phrygians and Lydians); Persia; Phoenicia (Syria) and Palestine. India and China have been omitted, because, as explained, the knowledge of the early civilisations of these countries is at present so very incomplete. The book stops short of the later civilisations of Greece and Rome.

For the sake of clearness and simplicity the subject-matter is dealt with under different heads, namely, historical and general; metals and non-metals.

The reviewer has only praise for the book, which is, and must remain for many years, the most complete account of this particular subject, and, if he ventures to criticise it, or rather to comment upon it, this is not done in any carping spirit, but with the hope that future editions may be still more complete and valuable. The main comment is that, since the author is not acquainted at first hand with the objects and materials described, he has necessarily been obliged to rely upon the written accounts of others, and, therefore, he has not been able to assess the accuracy and value of the descriptions, except in a few instances, where, as a chemist, he has detected some chemical impossibility. For instance, in the Egyptian section, Breasted, Budge, Erman-Ranke, Maspero, Wilkinson, and others are frequently quoted for the nature of certain materials, and, although these writers are (or were) all very eminent in their own special lines of work, they are (or were) literary men—philologists and historians—and not practising archaeologists, and it is not to be wondered at, therefore, that their statements respecting the nature and composition of materials are frequently wrong. Even archaeologists have sometimes been mistaken, for it is only in recent years that the chemist and geologist have been regularly consulted in archaeology, and the literature of the subject is full of mistaken identifications of materials. Thus, to take a few examples from the present book, that copper or bronze was ever gilded by applying gold leaf with "an ammoniacal solvent" (p. 25) is most improbable; the gold earrings of Rameses XIIth are not "covered with a rich red-brown varnish" (p. 29); that the pupils of the eyes of the Sheikh el-Beled are of ebony (p. 42) has not been proved, and is almost certainly wrong. (Incidentally this statue is not of the Third Dynasty, as stated, and not from any pyramid at Saqqâra). That much of the "red granite" described by Egyptologists is really a hard sandstone breccia (p. 101) is not so, nor are there any quarries of such stone on the Kossayr road; that "true red granite" was not much used after the First Dynasty (p. 102) is surely a misprint, since in the construction of the Fourth Dynasty pyramids at Giza there is a considerable amount of this stone; that the eyes of mummies were made of all the various materials enumerated (p. 121) is incorrect, though some of these materials were employed for certain parts of eyes, but no evidence can be found for the use of others; orpiment, stated not to have been employed as a pigment (pp. 137–9), was used during the XVIIIth and XIXth Dynasties; that sawdust could be identified as from the Atlas cedar, as distinguished from the cedar of Lebanon (p. 194), is very doubtful; and that traces of alcohol should have been found in mummy tissue (p. 198) is practically impossible.

The author is under a misapprehension in thinking that the reviewer has stated that a mixture of resin and fat was applied to mummies before treatment with natron (p. 173), and that Canopic jars probably contained natron solution (p. 176), since only one instance is known of natron solution in a Canopic jar and one in a Canopic box.

The use of the obsolete word carneol for carnelian occurs three times (pp. 29, 132, 382). Asi is accepted as meaning Cyprus (p. 363), though Wainwright has shown that this is almost certainly wrong.

The mistakes mentioned, however, are comparatively small matters and do not affect the general excellence of the book.

The publishers are to be congratulated in that the book is so clearly printed and well produced, and that it is free, or practically free, from printer's errors, speaks well for the proof-reading.

A. LUCAS

OPTICAL ROTATORY POWER. By T. MARTIN LOWRY, C.B.E., M.A., D.Sc., F.R.S. Pp. xiii + 483. London: Longmans, Green & Co. 1935. Price 30s.

It is thirty-seven years since the second and last edition of Landolt's *Das Optische Drehungsvermögen* was published, but the theoretical foundations of the phenomenon of optical activity had been so well and truly laid by Pasteur, le Bel and van't Hoff, that the book can hardly be regarded as quite out of date. It is out of print, however, and so much work has been done since its publication in amplification and extension of le Bel and van't Hoff's theory of the tetrahedral configuration of compounds of the methane type, that a new and authoritative book on optical activity will be warmly welcomed.

A comparison of "Landolt" with Professor Lowry's book shows, very strikingly, the great progress that has been made in this field of physical chemistry. Hence, the number of elements from which optically active compounds have been prepared has been increased from two (carbon and nitrogen) to twenty-one, largely owing to the work of Sir W. J. Pope. The optical activity associated with the non-metallic elements and with some of the metals (beryllium, zinc and copper) is explained, on the basis of the tetrahedral model, by recent developments of the valency theory; thus, asymmetric ammonium salts are now represented as containing a quadricovalent ion comparable with methane. The optical activity associated with other metals is ascribed to the octahedral model proposed by Werner in 1892 as a spatial representation of metallic radicals in co-ordination compounds of the cobaltammine type; the preparation, by Werner in 1911, of optically active compounds of this kind is a conclusive proof of the validity of the octahedral model. The prediction by van't Hoff of the discovery of optical activity in dissymmetric molecules, even in the absence of an asymmetric atom (*e.g.* allene derivatives), was fulfilled in 1909 by Perkin, Pope and Wallach, who resolved 1-*methyl* cyclo *hexylidene*-4-*acetic acid.*

Professor Lowry discusses the nature of rotatory dispersion and the measurement of dispersion in the visible, ultra-violet and infra-red parts of the spectrum at considerable length; it is pointed out that the relative ease with which the nearly monochromatic light of the sodium flame is obtained led to the comparative neglect of the study of rotatory dispersion for many years.

With regard to polarimeters, to which a chapter is devoted, no new features of importance are recorded; indeed the half-shadow polariser devised by Lippich fifty years ago satisfies the requirements of the most exact work. In the short chapter on saccharimeters it is stated that "The vernier is constructed to read to 0·1° sugar, which corresponds to a rotation for sodium light of 0·034657°." This is the value for the rotation as determined by O. Schönrock in 1904, and subsequently used in the quartz plate calibration of the Ventzke scale. More recent determinations by Bates and Jackson, Stanek, and Kraisy and Traegel indicated that Schönrock's value was too high, and in 1932 the International Commission for Uniform Methods of Sugar Analysis adopted the value 0·034620 as the basis for calibrating the "International Sugar Scale."

Other chapters deal with circular dichroism, magnetic rotation and the optical activity displayed in various classes of organic compounds. The book concludes with a very full account of the various theories of optical rotation and dispersion.

The book is written in a very easy, lucid style, and is remarkably free from errors even of a kind too trivial to mention. It will certainly rank as the standard work on a subject to which Professor Lowry's own researches have contributed so much.

LEWIS EYNON

APPLIED CHEMISTRY. A PRACTICAL HANDBOOK FOR STUDENTS OF HOUSEHOLD SCIENCE AND PUBLIC HEALTH. By C. KENNETH TINKLER, D.Sc., F.I.C., and HELEN MASTERS, B.Sc. Volume I: Water, Detergents, Textiles, Fuels, etc. Third Edition, revised. Pp. xii+296. London: The Technical Press, Ltd., 5, Ave Maria Lane, Ludgate Hill, E.C.4. 1935. 15s. net.

The sub-title of this book is a necessary limitation of its very broad main title. Though the scheme of the book is chemical, some purely physical subjects, such as hygrometry and the determination of calorific values, are included; but their introduction is logical and governed by the explanation in the preface to the first edition that it is the authors' aim to provide a theoretical and practical course not otherwise obtainable in a single text-book.

The scope of the book may be indicated by a rough division into Water Analysis, Water Softening, Soap, Textile Fibres, Bleaching and Dry-cleaning Agents, Air Analysis, Fuels, Coal Tar Disinfectants, and Protective Agents (Paints, etc.). The treatment is thoroughly practical, all the experiments being well-chosen typical laboratory operations. Much of the work is analytical, and the theoretical principles underlying each experiment are fully and lucidly explained, a noteworthy exception being the omission to inform the student that the compound $Na_2S_4O_6$ occurring in the equation for the reaction between iodine and sodium thiosulphate is sodium tetrathionate.

Though the theory of hydrogen ion concentration is admittedly beyond the scope of the book the student might have been introduced to the popular "universal indicator" as a better means of determining the reaction of drinking water than the suggested use of litmus paper. Exception must be taken to the statement on p. 10 that "as a rule the amount of chlorine as chloride per 100,000 present in a drinking water does not exceed 2 parts." The ortho-tolidine test for the determination of free chlorine in chlorinated water receives scantier treatment than it deserves.

The bulk of the subject-matter has been brought up to date in this edition and there are numerous references to text-books and reports. It is difficult to understand why, in the description of Boys's Calorimeter, the reader is referred to the Gas Referees' Notification of 1918, a publication probably not easy to obtain. The current Notification is that of November 15th, 1933, a subsequent Notification of August 31st, 1934, being a modification of certain provisions of the 1933 Notification and only of interest to official gas examiners.

An initial chapter-index with subdivisions and a terminal combined name- and subject-index are provided. The terminal index deals adequately with the major and minor subject-matter of the text, but is deficient in its references to incidental information which is scattered throughout the book. Thus Westropol, Tetrapol and Rongalite (the last referred to the page previous to that upon which it occurs) are included, but the equally important Tetraline and Sextol and their chemical synonyms are omitted.

Except for an obvious and immaterial error in the calculation on p. 286 the book appears to be free from misprints. On p. 184 the unusual spelling "mille-calories" occurs three times. There are numerous diagrammatic sketches of apparatus and two plates of excellently reproduced photomicrographs of textile fibres.

As a course of instruction the book cannot fail to achieve its purpose and can confidently be recommended not only to students taking the degree course in Household and Social Science in London University for whom it is primarily intended, but to all students interested in the applications of chemistry to matters of domestic and hygienic importance. To the advanced industrial and analytical chemist its interest will lie in its items of incidental information rather than in its gross subject-matter, but the chapter on Textile Fibres will be found useful by all who are not specialists in this subject.

A. O. JONES

THREE PHILOSOPHERS (LAVOISIER, PRIESTLEY AND CAVENDISH). By W. R. AYKROYD. Pp. xii+227. With 8 illustrations. Heinemann (Medical Books). 1935. Price 10s. 6d. net.

The sub-title of this book, in spite of its rather misleading main title (for the scientist appears to have lost his eighteenth-century prerogative to the name of philosopher), should be sufficient to indicate to analysts that the subject of Dr. Aykroyd's study concerns the very foundations of their craft. If, moreover, they have been so wise as to have read the author's even more unfortunately titled "Vitamins and other Dietary Essentials" (see ANALYST, **58**, 1933, 428), they will expect a racy, well-informed, entertaining and penetrating study. They will not be disappointed.

Lavoisier is the centre of the author's triptych, and he keeps him well in the middle of the picture, skilfully supported by equally convincing, if slighter, studies of Priestley, the rugged nonconformist, and Cavendish, the aristocratic misanthrope. It is difficult to imagine three men more fundamentally divided in origins and, perhaps partly in consequence, more diverse in outlook and temperament. The immense unifying power of that exalted inquisitiveness we call science is perhaps the only agent in the world that could have given them common interests and actually caused them to make contact: even art would have been too dependent on a certain anarchy of spirit to achieve such a *rapprochement*.

Dr. Aykroyd is sufficiently a humanist, his objective outlook notwithstanding, for neither Lavoisier to appear to him the complete Sydney Carton of science, nor the revolutionaries the ultimate embodiment of sub-human malevolence. After all, he is an Irishman; his native rebellious instincts and his native sense of humour alike would forbid him such melodramatic distortions. He sees Lavoisier as the representative, albeit exceptionally intelligent and disinterested, of an oppressor class; he sees the Tribunal, even the hated Fouquier-Tinville, certainly the Marats, the Robespierres, the Dantons and still more the non-commissioned ranks, as the spokesman, whatever their individual motives, of a desperate and unappeasable popular rising. The execution of Lavoisier was a crime of catastrophic seriousness for the advance of human knowledge, but for the humanitarian it was no more tragic, and no less, than the deaths of the many thousands who died of starvation under the regime of the Farmers General, or perished later in destroying that regime at the barricades.

It must not be thought that Dr. Aykroyd's account of Lavoisier, or of Priestley and Cavendish, is confined to matters scientific and sociological; his book is full of minor incidents, revealing this or the other quaint facet of his characters. The tale of the Abbé La Caille's meticulous accountancy is not the least piquant of his adventitious anecdotes.

It is a pity that Lewis Carroll did not invent an un-Christmas present while he was about inventing the un-birthday present. Let us make good the deficiency with the excellent excuse provided for us by Dr. Aykroyd. I strongly recommend every analyst who wishes to be reminded of the early days of chemical science, and reminded in a way that will give at least as much entertainment as re-instruction, to treat himself to a copy of *Three Philosophers* as an un-Christmas present.

A. L. BACHARACH

A TEXTBOOK OF QUANTITATIVE CHEMICAL ANALYSIS. By A. C. CUMMING and S. A. KAY. Pp. 482. Sixth Edition. Revised by F. C. GUTHRIE and J. T. NANCE. London: Gurney & Jackson. 1934. Price 15s.

"Cumming and Kay" is one of the accepted textbooks for University and College students, and therefore a new edition is of considerable interest. Owing to the rapid advance in inorganic analysis, a substantial amount of revision has been necessary to bring the book up to date. The revisers have performed their task commendably, and, without increasing the size of the book to any extent, have found room for much new matter by eliminating a former section on molecular weight determination, and omitting certain methods, such as the determination of copper as sulphide, which are becoming obsolete.

The book is entirely practical in scope and gives a clear account of analytical technique. The ml. has been adopted. About 200 pages are occupied with volumetric processes and typical gravimetric exercises. Various methods which are now in the stage of gaining general acceptance are included, such as those based on the use of internal indicators in dichromate titrations and in the ferrocyanide titration of zinc, zinc amalgam as a reducing agent, and absorption indicators in halide titrations. Electrometric methods as applied to *p*H determination, acid-alkali and oxidation-reduction titrations are described from the practical standpoint in a way which should provide a valuable introduction to this growing field of work, the aim having been to show how the methods may be used in the simplest possible way. In connection with colorimetry, well-chosen modern methods appear, as, for example, the aurintricarboxylic acid method for small amounts of aluminium and the glyoxime-hypochlorite method for traces of nickel. A colorimetric method which one might expect to find, *viz.* the iodide method for bismuth, is, however, unaccountably absent. In the section on electrodeposition methods, procedures for copper, nickel, zinc, etc., are given, and it may be noted, for example, in connection with copper, that the necessary steps to ensure complete deposition are pointed out, namely, reducing the current density towards the end of the process and adding urea to destroy nitrous acid. One is impressed again by the selection of good modern methods of gravimetric analysis. Thus, for magnesium, the improved method for precipitating magnesium ammonium phosphate devised by Epperson is adopted, and Berg's 8-hydroxyquinoline precipitation is described. A notable omission however, is, that of the zinc uranyl acetate method for sodium, by which sodium may be precipitated from quite complex mixtures in such a form that it may be weighed or determined volumetrically; because this method removes sodium from the unenviable position of nearly always having to be determined by difference, it would appear well to deserve prominence.

In connection with gravimetric precipitations much useful information is given as to the appropriateness and limitations of precipitation methods when used to separate elements from mixtures, and an "index of separations" is given at the end of the book for easy reference. The fact that the authors well appreciate the troubles which arise in the quantitative analysis of mixtures is evidenced by the following quotation: "One of the most difficult problems met with in quantitative analysis is the selection of good methods of separation. A perfect separation is rarely obtained by the methods adopted in qualitative analysis; these methods are often quite unsuitable, or require modification, for the purposes of quantitative analysis." Happily, the position is being steadily improved as more specific methods are brought to light.

There are sections covering about 250 pages on the analysis of simple ores and alloys, etc., including steel and portland cement, gas analysis, water analysis, and elementary organic analysis. This part of the book will provide the student with the opportunity of gaining the experience required to deal with practical problems.

S. G. CLARKE

Publications Received

ORGANIC SYNTHESES. Vol. XV. Edited by W. H. CAROTHERS. Pp. v + 104. London: Chapman & Hall. Price 8s. 6d. net.

LABORATORY MANUAL OF PHYSIOLOGICAL CHEMISTRY. 3rd Ed. By M. BODANSKY and M. FAY. Pp. vii + 274. London: Chapman & Hall. Price 10s. net.

BIOCHEMICAL LABORATORY METHODS. By C. A. MORROW. Revised and rewritten by W. M. SANDSTROM. Pp. xv + 319. London: Chapman & Hall. Price 18s. 6d. net.

TEXTBOOK OF QUANTITATIVE ANALYSIS. 2nd Ed. By W. T. HALL. Pp. ix + 350. London: Chapman & Hall. Price 15s. net.

THE B.D.H. BOOK OF REAGENTS FOR "SPOT" TESTS AND DELICATE ANALYSIS. 4th Ed. Pp. viii + 82. London: The British Drug Houses, Ltd. Price 2s. 6d.

STANDARD METHODS FOR TESTING PETROLEUM AND ITS PRODUCTS. 3rd Ed. Pp. xi + 228. London: The Institution of Petroleum Technologists. Price 7s. 6d. net.

AUGUST, 1935 Vol. 60, No. 713

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

THE Sixth Summer Meeting was held at the Queen Hotel, Harrogate, from June 21st to 24th. The attendance was sixty, including many ladies.

The Chairman (Prof. W. H. Roberts) presided, and among those present were Past Presidents (Dr. Dyer accompanied by Mrs. Dyer, Mr. E. R. Bolton, and Mr. E. Hinks with Mrs. Hinks), the Hon. Treasurer (Dr. E. B. Hughes with Mrs. Hughes), the Hon. Secretary (Dr. Roche Lynch), the Editor of THE ANALYST (Dr. C. A. Mitchell), Miss Elliott, Mr. A. Lucas and Miss Enid Bradford, from the South; and Dr. T. W. Drinkwater (Vice-Chairman of the newly-formed Scottish Section), Mr. J. B. McKean (Hon. Secretary, Scottish Section), Mr. A. R. Jamieson and Dr. Dryerre.

The Chairman extended a cordial welcome to all members attending, especially those from the South, and the four representatives of the Scottish Section.

Mr. A. Woodmansey, Analyst to the Harrogate Corporation, read a paper on Saturday morning on "The Mineral Waters of Harrogate."

A vote of thanks to the lecturer was proposed by Mr. H. M. Mason, and seconded by Mr. G. D. Elsdon.

A resolution expressing the cordial greetings of the Section, and affirming its continued loyalty to the Council of the parent Society, was unanimously passed on the motion of Mr. C. J. H. Stock, seconded by Mr. G. D. Elsdon.

Telegrams were sent to the following members who were prevented, through illness, from attending the meeting: The President (Mr. John Evans), Past-President (Dr. J. T. Dunn), Vice-Chairman of the Section (Mr. A. R. Tankard), and the Hon. Secretary of the Section (Mr. J. R. Stubbs).

The party visited the Grand Opera House on Saturday evening, and on Sunday a visit was made to Fountains Abbey, where Dr. Moody, Organist of Ripon Cathedral, gave a most interesting account of the history of the Abbey. Tea was afterwards taken at Brimham Rocks.

Dr. Drinkwater expressed, on behalf of the Scottish members present, appreciation of the welcome and hospitality extended to them by the Section.

In the absence of Mr. J. R. Stubbs, the duties of Hon. Secretary were carried out by Mr. Arnold Lees.

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXIX. The Separation of Tungsten from Titanium, Niobium, Tantalum, and Zirconium

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IN an earlier Section, Schoeller and Jahn[1] have shown that tungsten cannot be included in any of the groups obtained in our proposed scheme for the analysis of earth-acid minerals, because it is partially precipitated with the earth acids by tartaric hydrolysis, as well as by tannin and by cupferron from tartrate or oxalate solutions. Hence there arose the need for a method which would quantitatively separate small amounts of tungsten from large amounts of earth acid as well as from associated earths, chiefly titania and zirconia. It was mentioned in the paper referred to above that such a method had been worked out. This Section contains a description of the procedure (which is based upon Bedford's work[2] on the separation of tungsten from niobium) and an account of our investigations into the separation of tungsten from titanium.

A. SEPARATION OF TUNGSTEN FROM TITANIUM.—Of all the metallic oxides which occur in earth-acid minerals, tungstic oxide alone forms stable, soluble alkali salts. The more basic earths are unaffected by alkali,[3] whilst the earth acids form sodium salts which are sufficiently insoluble to be used for the separation of tungsten from tantalum and niobium.[4] Titania appears to hold an intermediate position between the earth acids and the more basic earths, since Schoeller and Deering[5] have shown that its behaviour in an alkali fusion is strongly affected by association with niobic oxide. Hence an inquiry into the separation of tungsten from titanium formed the first step in this investigation.

No deviation from time-honoured practice could be found by reference to recent literature. The few published methods need not be discussed here, the essential information being fairly summarised in the following passage taken from Bull. 212 of the U.S. Bureau of Mines[6]: "The separation of Ti from W presents little difficulty, so that both may be easily determined in the same sample. Fusions with alkalis, followed by water leach of the melt, offer a simple method for the separation. The W is obtained in the filtrate, while the Ti remains in the residue. In the fusion with pyrosulphate the conditions are reversed, in that the W remains in the insoluble residue as WO_3, and the Ti passes into the filtrate as the sulphate. This separation is best accomplished if a few drops of concentrated H_2SO_4 are added to the H_2O in which the pyrosulphate fusion is dissolved. This precaution assists in keeping the W in the insoluble portion."

We considered it necessary to investigate the effect of these procedures on oxide mixtures of low tungsten-content.

(*a*) *Pyrosulphate fusion.*—The mixed oxides were fused with potassium pyrosulphate (3 g.), and the product was leached with 5 per cent. sulphuric acid (Exp. 1). The melt dissolved to a *perfectly clear solution.* The liquid was then treated with cinchonine solution and warmed, but even this specific reagent did not induce a normal tungsten precipitation. The small precipitate obtained overnight (0·0080 g.) contained more titanium than tungsten.

This single experiment disposes of the procedure under discussion as a means for separating tungsten from titanium. No doubt, with oxide mixtures of low titanium-content, tungstic acid may remain substantially insoluble but, we venture to predict, contaminated with titania. The case is plainly analogous to that of titania in association with the earth acids[7]: if tantalum and niobium, whose power of forming soluble complexes is weak, undergo "loss of individuality" when associated with sufficient titanium, then tungsten, a complex-former *par excellence*, may be expected to behave as it did in the above experiment, when it dissolved to a clear solution which gave a negative reaction for tungstic acid, even with cinchonine. Rose[8] was aware of the ineffectiveness of the pyrosulphate separation process. He states that in the lixiviation of the melt the titania dissolves first, but that subsequently the tungstic oxide also dissolves (complex-formation). He resorts to treatment of the solution with ammonia, although the titanium precipitate thus produced occludes tungstic acid.

Exp.	WO_3 g.	TiO_2 g.	
1	0·0224	0·2028	WO_3 recovery: Nil
2	0·0546	None	,, ,, Nil
3	0·0220	0·1040	R^1: 0·0288 g. R^2: 0·0216 g.

In Exp. 2 pure tungstic oxide was fused with bisulphate, and the product was lixiviated with water. The cloudy liquid thus obtained cleared completely on warming, and remained clear while boiling. After cooling, it gave a characteristic precipitate with cinchonine solution. This test proves that, even by itself, tungstic oxide does not remain insoluble after bisulphate fusion. Re-fusion of the bisulphate melt of 0·0534 g. of tungstic oxide with 1 ml. of strong sulphuric acid previous to leaching led to the same result.

In Exp. 3 we tested the application of the pyrosulphate and tannin method[9] to this separation case. The tannin prevented the formation of a soluble tungsten complex just as in the case of the earth acids and titania,[9] but the weight of the ignited residue, R^1, was excessive; re-treatment of R^1 gave a seemingly good result, but R^2 was still contaminated with 2 to 3 mg. of titania. The tests with pyrosulphate were then abandoned.

(*b*) *Alkali fusion.*—In Exps. 4 to 8, sodium carbonate was used as flux. The mixed oxides were fused with 3 g. of this salt until the fused mass was quite clear. The cold mass was extracted with water in Exp. 4, and with half-saturated sodium chloride solution in Exp. 5. In each case the tungsten recovery showed a negative error of about 40 per cent., and the titania residue gave a positive tungsten reaction. Hence the other procedure recommended in the above quotation was also found to be defective.

Exp.	Taken		Tungstic oxide		Titania	
	WO_3 g.	TiO_2 g.	Found g.	Error g.	Found g.	Error g.
4	0·0205	0·2010	0·0126	−0·0079		
5	0·0212	0·2043	0·0130	−0·0082		
6	0·0200	0·2030	0·0202	+0·0002	0·2034	+0·0004
7*	0·0360	0·1685	0·0362	+0·0002	0·1686	+0·0001
8*	0·0061	0·2387	0·0056	−0·0005	0·2386	−0·0001

* Quantities taken not known to operator.

Re-treatment of the titania residue by the same process did not recommend itself, in view of the very imperfect separation achieved by the first fusion. We inferred that occlusion of tungsten by the titania during lixiviation might be counteracted by the use of caustic alkali instead of water. Experiments in this direction proved successful at fairly high alkali concentrations (*i.e.* 10 per cent. sodium hydroxide; see Exps. 6, 7). The separation was carried out as follows:

(*c*) *Authors' caustic-soda method.*—The mixed oxides (about 0·25 g.) are fused with 3 g. of sodium carbonate in a platinum crucible over a Teclu burner for 20 minutes or until the fused mass is clear. The cold crucible is transferred to a nickel dish containing a solution of 10 g. of sodium hydroxide in 50 ml. of water. The covered dish is kept on a boiling water-bath for 2 to 3 hours, the water lost by evaporation being replaced. The crucible is cleaned and rinsed with 50 ml. of hot water. The liquid is allowed to stand until cold or overnight, and filtered. The residue, P^1, is washed with half-saturated sodium chloride solution, and reserved.

The filtrate is submitted to bicarbonate hydrolysis,[10] *i.e.* treatment with phenolphthalein indicator and dilute hydrochloric acid until the red colour disappears. The solution is heated on the water-bath, the red colour being discharged from time to time with a few drops of acid. The small flocculent precipitate, P^2, is collected, and washed in the same way as P^1.

The filtrate from P^2 is treated with 0·5 g. of tannin,[11] etc., for the determination of the tungstic oxide. For the quantitative recovery of the titania, the filters containing P^1 and P^2 are pulped with a little *N* hydrochloric acid. After dilution to 100 ml., the liquid is warmed and made slightly ammoniacal; the precipitate is collected, washed with ammonium nitrate solution, and ignited. It is advisable to leach the ignited precipitate, unless small, with a little dilute acid; after addition of a slight excess of ammonia, the precipitate is again collected, ignited strongly, and weighed.

It will be noted that Exp. 8 gave a less complete tungsten recovery, which we ascribe to the use of caustic alkali of one-half the strength specified above.

B. SEPARATION OF TUNGSTEN FROM TITANIUM, NIOBIUM, TANTALUM, AND ZIRCONIUM.—Having quantitatively separated tungsten from titanium by our caustic-soda method, we proceeded to apply the method to the separation of tungsten from large amounts of titanium and niobium. The case is of importance in its application to titanoniobate minerals (*e.g.* samarskite).

The method applied to that ternary mixture proved a failure, because of the modified behaviour of titania and niobic oxide in association. Each oxide without the other remains insoluble in the treatment; but a mixture of the two in approximately equal quantities gives a considerable fraction soluble in caustic soda to a semi-colloidal solution which is not completely flocculated by bicarbonate hydrolysis. Exp. 9 illustrates the course of an attempted separation:

		Taken		
Exp. 9	TiO_2	0·1202 g.	P^1:	0·1630 g.
	Nb_2O_5	0·1244 ,,	P^2 (contains Ti and W): ..	0·0720 ,,
	WO_3	0·0304 ,,	Tannin-cinchonine ppte.: ..	0·0406 ,,
	Σ	0·2750 ,,	Recovery:	0·2756 ,,

Exp. 10, in which a small addition of tantalic oxide was made, gave the same result:

Taken				
TiO_2 0·1070 g.;	Nb_2O_5 0·1139 g.	Tannin-cinchonine ppte.: 0·0236 g.
Ta_2O_5 0·0325 ,, ;	WO_3 0·0134 ,,	

After experimenting with various other schemes, we turned our attention to the action of ammoniacal magnesium solutions upon alkaline solutions of the metallic acids. Bedford,[2] who first applied the reaction in the analysis of a niobotungstate, found that it precipitates the niobic acid, the alkali tungstate remaining in solution. He determined the niobium in the ignited precipitate by fusing it with bisulphate and extracting the product with boiling water. He did not attempt the recovery of the tungstic oxide, the quantity of which he obtained by difference.

We succeeded in utilising Bedford's reaction for the separation of tungsten from titanium and niobium, recovering the two earths as a mixed tannin precipitate, and determining the tungsten by our tannin and cinchonine method (Exps. 12 to 14). The whole process, which will be referred to as the *Magnesia Method*, is fully described under C below. (The results obtained are shown on page 510.)

The niobium experiments (12 to 14) were more satisfactory than the test separations of ternary mixtures containing tantalic oxide (15 to 17). In Exp. 15, a single treatment gave a negative tungsten, and a positive tantalum, error; this was again the case in Exp. 16 (WO_3 error $-0{\cdot}0016$, Ta_2O_5 error $+0{\cdot}0016$ g.), but re-treatment of the ignited TP^1 (0·4090 g.) gave the final errors recorded in the Table. As for Exp. 17, the separation succeeded in one treatment, in which the precipitant was added at about 50° C., and the further heating of the suspension of the magnesia precipitate was omitted (*infra*, under C).

The more complex mixtures of Exps. 18 and 19 were successfully treated in a single operation; this we ascribe to niobic oxide forming a substantial proportion of the mixed earths (as in Exps. 12 to 14), zirconia not interfering in the magnesia method (see Exps. 26, 27).

C. THE MAGNESIA METHOD.—The mixed oxides (0·2 to 0·5 g.) are fused with 4 g. of potassium carbonate in a platinum crucible over a strong burner for 10 to 15 minutes. The fused mass is taken up in 200 ml. of hot water, care being taken to disintegrate any lumps by gentle boiling and manipulation with a glass rod. The crucible is rinsed and discarded, and the hot solution is treated with freshly-prepared reagent (1 g. of crystallised magnesium sulphate, 2 g. of ammonium chloride, 25 ml. of water, 4 drops of ammonia). The covered beaker is kept on a covered water-bath for an hour. The flocculent precipitate is collected on an 11-cm. No. 40 Whatman filter, and washed with quarter-saturated ammonium chloride solution.

Exp.	Earths taken	g.	Tungstic oxide taken g.	Amounts found g.	Error g.
11	None		0·0310	0·0311	+0·0001
12*	TiO_2	0·1547	0·0324	0·0320	−0·0004
	Nb_2O_5	0·1546			
	Σ	0·3093		0·3095	+0·0002
13*	TiO_2	0·2130	0·0341	0·0337	−0·0004
	Nb_2O_5	0·2074			
	Σ	0·4204		0·4202	−0·0002
14*	TiO_2	0·1040	0·1016	0·1008	−0·0008
	Nb_2O_5	0·1036			
	Σ	0·2076		0·2084	+0·0008
15*	TiO_2	0·2027	0·0242	0·0225	−0·0017†
	Ta_2O_5	0·2032			
	Σ	0·4059		0·4072	+0·0013†
16*	TiO_2	0·2052	0·0225	0·0228	+0·0003‡
	Ta_2O_5	0·2026			
	Σ	0·4078		0·4073	−0·0005‡
17*	TiO_2	0·2027	0·0228	0·0228	0·0000†
	Ta_2O_5	0·2020			
	Σ	0·4047		0·4045	−0·0002†
18*	TiO_2	0·1153	0·0248	0·0243	−0·0005
	Nb_2O_5	0·2045			
	Ta_2O_5	0·1080			
	Σ	0·4278		0·4280	+0·0002
19*	TiO_2	0·0788	0·0315	0·0312	−0·0003
	Nb_2O_5	0·1134			
	Ta_2O_5	0·0902			
	ZrO_2	0·1020			
	Σ	0·3844			

* Quantities taken not known to operator.
† Single treatment } see text below.
‡ Double treatment } see text below.

Determination of the mixed earths.—The precipitate is rinsed back with the same wash-liquor; the filter is placed in the platinum crucible intended for the ignition of the tannin precipitate, TP^1. The suspension of the magnesia precipitate (150 ml.) is acidified with hydrochloric acid and digested on the water-bath for an hour. An equal volume of saturated ammonium chloride is then added, and the reaction is adjusted with ammonia to slight acidity to litmus paper. The liquid is now treated with 2 g. of ammonium acetate and heated to boiling, and fresh 5 per cent. tannin solution is added until flocculation is complete. The precipitate,

TP^1, is allowed to settle on the water-bath, collected with the help of gentle suction, washed with the ammonium chloride solution, and ignited with the filter from the magnesia precipitate.

If TP^1 requires re-treatment, it is again fused with potassium carbonate, and the operations above described are repeated, yielding a second magnesia precipitate and a filtrate therefrom, which is added to the first. The magnesia precipitate is again treated with tannin as for TP^1, giving TP^2, which is ignited, leached as usual,[12] and weighed as mixed earths.

Determination of the tungsten.—The filtrate or combined filtrate from the magnesia precipitate or precipitates is treated by the tannin and cinchonine method. This procedure, as originally described, is carried out in a solution of high sodium chloride concentration; in the magnesia method we add a filtered, hot-saturated solution of 20 to 30 g. of ammonium chloride before precipitating the tungsten complex.

D. COMPARATIVE TESTS ON THE SEPARATION OF BINARY MIXTURES BY THE METHODS DESCRIBED.—Having solved the most complex of the above-mentioned separation problems by the use of the magnesia method, we surmised that it might do duty as a general method applicable to all the separation cases under discussion. Exps. 20 to 28 were carried out with a view to deciding that question.

Exp.		Taken	Found in		Final errors
			first treatment	re-treatment	
		g.	g.	g.	g.
20	WO_3	0·0337	0·0281	0·0047†	−0·0009
	TiO_2	0·2078			
21*	WO_3	0·0320	0·0306	Not done	−0·0014
	TiO_2	0·2614			
22*	WO_3	0·0236	0·0266	0·0235‡	−0·0001
	Nb_2O_5	0·2536			
23*	WO_3	0·0307	0·0328	0·0308‡	+0·0001
	Nb_2O_5	0·2140			
24	WO_3	0·0259	0·0247	0·0011†	−0·0001
	Ta_2O_5	0·2274		0·2271†	−0·0003
25	WO_3	0·0229	0·0213	0·0016†	0·0000
	Ta_2O_5	0·2056		0·2051†	−0·0005
26*	WO_3	0·0316	0·0320		+0·0004
	ZrO_2	0·2898			
27*	WO_3	0·0147	0·0150		+0·0003
	ZrO_2	0·2783			
28*	WO_3	0·0320	0·0296	Not done	−0·0024
	TiO_2	0·1822			
	ZrO_2	0·2206			

* Quantities taken not known to operator.
† Obtained by re-treatment of TP^1.
‡ Obtained by re-treatment of WO_3 product.

Exps. 20 to 25 prove that the separation of tungsten from the three individual earths in one operation is less satisfactory than that from the mixed earths: titania and tantalic oxide both occluded tungsten, whilst the precipitation of the niobic oxide by the magnesia reagent was not quite quantitative. Re-treatment of *TP*[1] in Exps. 20, 24 and 25, and of the ignited tannin-cinchonine precipitate in Exps. 22 and 23, gave good results. The mixture of titania and zirconia in Exp. 28 comported itself like titania. The separation of tungsten from zirconium by the magnesia method (Exps. 26, 27) is satisfactory.

In order to obtain data for subsequent discussion (see E), we also carried out a few more tests by the caustic-soda method:

Exp.		Taken g.	Found g.	Errors g.
29*	WO_3	0·0156	0·0158	+0·0002
	Nb_2O_5	0·2753	0·2742	−0·0011
	WO_3	0·0344	0·0341	−0·0003
	Ta_2O_5	0·2096	0·2083	−0·0013
31*	WO_3	0·0206	0·0208	+0·0002
	Ta_2O_5	0·2271	0·2276	+0·0005
32*	WO_3	0·0334	0·0369	+0·0035
	ZrO_2	0·2224	0·2175	−0·0049
33*	WO_3	0·0342	0·0358	+0·0016
	ZrO_2	0·2000	0·1960	−0·0040

* Quantities taken not known to operator.

The separation from niobium and from tantalum gave a satisfactory tungsten recovery in one operation; 10 g. of sodium hydroxide were used in the extraction of the melt. We were surprised to find that the method did not give a quantitative separation of tungsten from zirconia (Exps. 32, 33). This must be due to incomplete hydrolysis, in the strongly alkaline solution, of the sodium zirconate present in the melt. The small amount of zirconia which thus accompanies the tungsten into the alkaline filtrate is not precipitated therefrom by bicarbonate hydrolysis, and most of this soluble fraction becomes occluded in the tannin cinchonine precipitate. Hence the tungsten results show a positive, the zirconia results a larger negative, error. The above deduction was confirmed by Exps. 34 and 35, in which the oxides were fused with alkali carbonate, and the melt was extracted with hot water instead of caustic soda; the recovered tungstic oxide was now free from zirconia:

Exp.	WO_3 taken g.	ZrO_2 added g.	Flux	WO_3 found g.	Error g.
34*	0·0311	0·2045	Na_2CO_3	0·0306	−0·0005
35*	0·0328	0·2056	K_2CO_3	0·0328	0·0000

* Quantities taken not known to operator.

E. ANALYTICAL APPLICATION.—As a result of the experimental work here recorded, an appropriate method from amongst four can be selected for the quantitative separation of tungstic oxide from certain earths and mixtures thereof.

(*a*) The magnesia method is generally applicable to the separation of tungsten from titanium, niobium, tantalum, or zirconium, and from binary, ternary, and quaternary mixtures of these earths. The separation from zirconium alone is complete in a single precipitation. Although in our test analyses the separation of tungstic oxide from mixed earths containing a substantial proportion of niobic oxide was complete in one operation, we think it advisable to repeat the treatment in doubtful cases where the quantity of tungstic oxide exceeds a few mg. In fact, in accurate work the completeness of the separation should always be ensured by a repetition of the procedure. With oxide mixtures in which niobic oxide preponderates, the purity of the tungstic oxide should be tested by solution in caustic soda, filtration, and precipitation of the filtrate with tannin and cinchonine.

(*b*) Sodium-carbonate fusion and extraction with caustic soda (caustic-soda method) separates tungstic oxide from titania in one operation, also from niobic or tantalic oxide or both, but not from titania *plus* earth acid or from zirconia.

(*c*) Sodium-carbonate fusion and extraction with water separates tungstic oxide from zirconia, beryllia, ferric oxide, thoria, ceria, and yttria in one operation.[3]

(*d*) Sodium-chloride precipitation separates tungstic oxide from niobic or tantalic oxide or both,[4] and from mixed pentoxides containing subordinate amounts of zirconia,[17] the latter remaining unaffected.

Although, strictly speaking, the magnesia method could be applied in all the cases under review, we do not feel disposed to advocate it to the exclusion of the other three processes. The caustic-soda method (outside the province of earth-acid analysis) is the simplest means for the separation of tungsten from titanium. Sodium-carbonate fusion and extraction with water form a valuable procedure of extensive applicability.[18] Lastly, precipitation by sodium chloride is a specific earth-acid reaction which also permits of a rapid approximate volumetric determination of tantalum and niobium. Schoeller and Jahn, the originators of the volumetric method, rightly considered the results too wide to recommend it for the actual determination of the two elements.[10] We revert to it here because Britton and Robinson[14] have described the tannin separation of tantalum from niobium as "extremely difficult, requiring considerable experience and skill before accurate results can be obtained." We do not dispute that all fractionation processes as such are difficult, but we hold that the tannin method under discussion is comparatively easy, thanks to the characteristic colour changes which mark the progress of the fractionation. However that may be, we would remind operators not too familiar with the tannin separation that they may obtain a preliminary approximation, at the same time as a separation from tungsten, by converting the mixed pentoxides into the sodium salts, titrating the alkali in the precipitate, and recovering the oxides as explained in Section VI.[10] The weighed recovered oxides (P^1)[15], together with the small bicarbonate-hydrolysis precipitate (P^2), are then fused with bisulphate, etc., for the separation of tantalum and niobium by tannin.[16]

The following unpublished determinations, by Schoeller and Jahn, of "unknown" quantities of mixed oxides, illustrate the degree of approximation of which the volumetric method is capable. (See table on page 514.)

With the exception of Exp. 1, the tantalum results show a negative error. We ascribe this to adsorption of alkali by the 9 cm. filter paper used. If so, closer results should be obtained by filtration on a small pad of filter pulp or a sintered glass crucible.

Exp.	Taken g.	P^1 (ex NaCl ppt.) g.	0·1 N HCl ml.	Found g.	Errors g.
	Ta_2O_5 0·2816	0·5054	36·53	0·2865	+0·0049
	Nb_2O_5 0·2300			0·2251	−0·0049
	Ta_2O_5 0·2132	0·5182	39·95	0·2015	−0·0117
	Nb_2O_5 0·3102			0·3219	+0·0117
	Ta_2O_5 0·3510	0·4670	31·65	0·3433	−0·0077
	Nb_2O_5 0·1230			0·1307	+0·0077
	Ta_2O_5 0·1752	0·4879	38·12	0·1725	−0·0027
	Nb_2O_5 0·3220			0·3247	+0·0027
	Ta_2O_5 0·2822	0·4512	32·20	0·2708	−0·0114
	Nb_2O_5 0·1742			0·1856	+0·0114
	Ta_2O_5 0·1952	0·4640	35·62	0·1864	−0·0088
	Nb_2O_5 0·2747			0·2835	+0·0088

Summary.—A separation of tungsten from titanium cannot be achieved by fusion of the mixed oxides with bisulphate and extraction of the melt with water or dilute acid. Fusion of the mixed oxides with sodium carbonate and extraction with water is likewise ineffective, but extraction of the carbonate melt with 10 per cent. sodium hydroxide solution affords a quantitative separation.

The only procedure found to separate tungsten from titanium and niobium, with or without tantalum and zirconium, consists in fusing the mixed oxides with potassium carbonate, and treating the aqueous extract of the melt with a slightly ammoniacal magnesium salt solution; the earths are precipitated, whilst alkali tungstate remains in solution. A repetition of the procedure is necessary unless the mixed earths contain a large proportion of niobic oxide; for accurate work, however, double treatment is recommended in all cases. Zirconia may be separated from tungstic oxide by fusion with alkali carbonate and extraction with water. The applicability of the methods available for the separation of tungsten from the individual earths and from the mixed earths is discussed. If the mixed earth acids are separated from tungsten by sodium-chloride precipitation, titration of the alkali in the precipitate furnishes a preliminary approximate determination of tantalum and niobium.

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A Colorimetric Method for the Quantitative Measurement of Rancidity

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THE Kreis test for rancidity in fats[1] has been in common use for a considerable time, and even to-day, when a number of other tests for auto-oxidative rancidity changes are available, it continues to enjoy some measure of popularity. The substance present in rancid fats giving rise to the red colour in the Kreis reaction is epihydrinaldehyde (Powick).[2] There is evidence that this substance is produced by the formation of a double peroxide of oleic acid, followed by the breaking up of the fatty acid into heptylic aldehyde, the half aldehyde of pimelenic acid and the oxide of acrolein-β-carboxylic acid, which itself is converted to epihydrinaldehyde.

The Kreis test has usually been applied as "a hit or miss" indication. Either the hydrochloric acid layer underlying the ethereal phloroglucinol solution is red or it is not. Pritzker and Jungkunz[3] formed epihydrinaldehyde by the oxidation of a drop of an aqueous solution of acrolein with hydrogen peroxide and obtained the red colour when the Kreis test was applied. The test was sensitive to 10 mg. of aldehyde in 100 ml. of oil. Later, Täufel and Russow[4] (1933) prepared epihydrinaldehyde from its acetal and described it as a very volatile, unstable compound, melting considerably below 0° C. It was stated to be present in autoxidised fat in a bound and non-volatile form. In this work the sensitivity of the Kreis test was placed at 1 : 2,000,000, and the minimum amount of aldehyde detectable at $0{\cdot}5\gamma$.

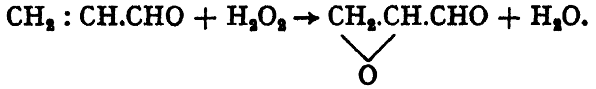
One of the main disadvantages in the use of the Kreis reaction is that a quantitative interpretation is difficult to obtain and often inaccurate. It is hard to avoid the formation of emulsions, and a considerable amount of oil is necessary (Taffel and Revis,[5] 1931; Lea,[6] 1934). This renders the test unsuitable for the examination of cereal products, where the oil must first be extracted before every test.

The following method for the quantitative measurement of rancidity was devised in the first place in order to investigate the auto-oxidative changes in the fat of wheat-germ. However, the method has also been used on other cereal and animal products and on a variety of oils, as such.

METHOD.—The oil (0·5 to 1 g.) is dissolved in sufficient of a 1 per cent. solution of phloroglucinol in acetone to give a 10 per cent. solution. A number of drops of sulphuric acid equal to the number of ml. of solution are added, and the mixture is placed in a water-bath at 10° C. for 15 minutes. The redness of the resulting colour is then determined by means of the Lovibond tintometer.

When a cereal product is being examined, the oil used has been extracted with ether. If, after standing, a precipitate appears, the solution is filtered directly into the tintometer cell through a dry paper.

Experimental.—It was considered logical to determine the conditions governing the accuracy of the test on epihydrinaldehyde itself. This substance was formed by the method of Pritzker and Jungkunz[8] by the oxidation of acrolein with hydrogen peroxide. The probable reaction is as follows:

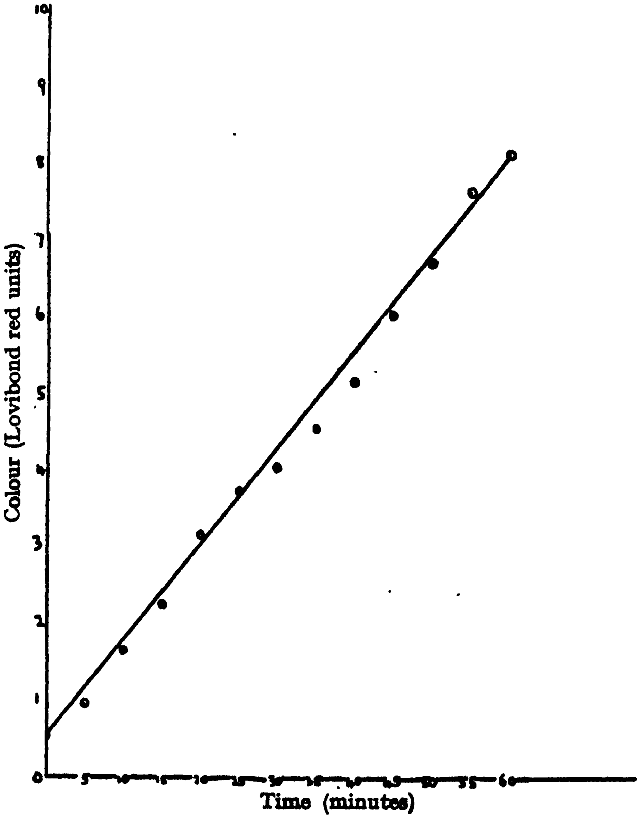


$$CH_2 : CH.CHO + H_2O_2 \rightarrow \underbrace{CH_2.CH}_{O}.CHO + H_2O.$$

(*a*) *The development of the colour in time.*—To 2 drops of a 1 per cent. aqueous solution of acrolein 2 drops of 6 per cent. hydrogen peroxide were added, followed by 5 ml. of the acetone and phloroglucinol reagent and 5 drops of sulphuric acid. As can be seen from Fig. 1, at room temperature the development of the colour is linear with time.

Fig. 1

The Development of Colour in Time



(*b*) *Effect of water on the development of the red colour.*—0·16 ml. of the 1 per cent. solution of acrolein in acetone was measured into 5 ml. of acetone and phloroglucinol reagent, water was added, and then 0·1 ml. of 6 per cent. hydrogen peroxide and 5 drops of sulphuric acid. The inhibiting effect of increasing amounts of water on the development of the red colour after 15 minutes' standing at room temperature is shown in Table I.

TABLE I

THE INHIBITION OF THE COLOUR BY WATER

Water added, ml.	0	0·03	0·06	0·09	0·12
Colour developed (Lovibond red units)	6·2	4·0	2·4	2·0	1·6

(*c*) *Effect of temperature on the development of the colour.*—0·16 ml. of the 1 per cent. solution of acrolein in acetone, 0·1 ml. of 6 per cent. hydrogen peroxide, and 5 drops of sulphuric acid were measured into 5 ml. of the acetone-phloroglucinol reagent, and the whole was allowed to stand for 15 minutes in a water-bath of known temperature. The effect of temperature on the development of the colour is shown in Table II. One solution, which was allowed to stand for the 15 minutes on a hot plate under a reflux condenser, gave a colour of 98 red units. This compares with 3·6 units at 12° C.

TABLE II

THE EFFECT OF TEMPERATURE ON THE DEVELOPMENT OF THE COLOUR

Temperature, °C.	2	12	18	23	24	25	28
Colour developed (Lovibond red units)	3·1	3·6	5·9	7·7	8·8	9·5	11·3

(*d*) *Concentration of sulphuric acid.*—The amount of sulphuric acid to be used was originally chosen at 1 drop for each ml. of solution, because this dilution usually gave a clear liquid with most of the fats examined. When the quantity of acid to be used came to be considered critically it at first appeared that the colour increased with increased acid in an S-shaped curve. This increase was later found to be due merely to the heating effect of the concentrated acid. At constant temperature the red readings when from 0·8 to 2·8 drops of sulphuric acid per ml. of solution (0·013 to 0·048 ml. of sulphuric acid per ml. of reagent) were used were practically the same, although at the higher concentrations the yellow component of the colour increased.

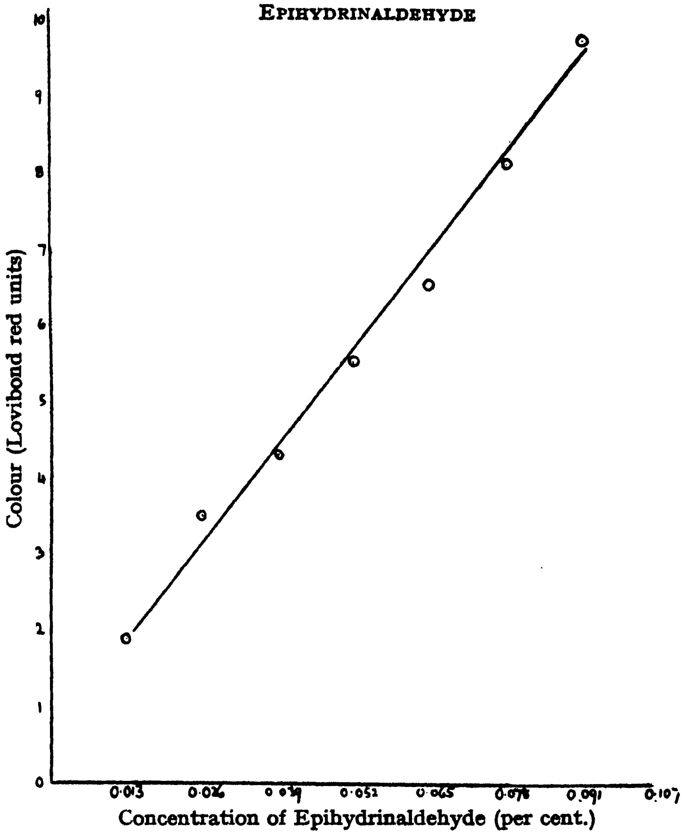
(*e*) *The effect of light.*—There was no difference in the depth of colour found between solutions exposed to the diffused illumination of a light laboratory and those allowed to stand in darkness.

(*f*) *Colour produced by varying amounts of epihydrinaldehyde.*—Drops of the 1 per cent. solution of acrolein in acetone and 0·1 ml. of 6 per cent. hydrogen peroxide were added to 5 ml. of the acetone and phloroglucinol reagent. In order to prevent the inhibition of the development of the colour by the water carrying the hydrogen peroxide, about 2 g. of anhydrous sodium sulphate were shaken with the solution. The solution was not filtered, but 5 drops (0·085 ml.) of concentrated sulphuric acid were added directly, and the whole was shaken well and allowed to stand for 15 minutes in a water-bath at a temperature of 10° C. After 15 minutes the liquid was decanted into the tintometer cell and the colour matched. The results are shown in Fig. 2.

SUMMARY.—From the foregoing work it appears that when the temperature is kept constant the depth of colour developed in a standard period of time by the reaction between epihydrinaldehyde, phloroglucinol and sulphuric acid in acetone solution is directly proportional to the amount of epihydrinaldehyde, provided that water is excluded. The following relationship between the depth of colour measured in Lovibond red units and the per cent. of epihydrinaldehyde present can be calculated from Fig. 2.

Fig. 2

THE DEPTH OF COLOUR PRODUCED BY MEASURED AMOUNTS OF EPIHYDRINALDEHYDE



Red units = 97 × (per cent. $C_3H_4O_2$) + 0·625,

Hence the lower limit of the method where a redness of 2 units is obtained would appear to represent a concentration of approximately 0·014 per cent. of epihydrinaldehyde.

When hydrogen peroxide or acrolein separately is allowed to stand with sulphuric acid and the acetone-phloroglucinol reagent, a faint yellow colour develops. After 15 minutes at 10° C. the red component of the colour produced by 0·3 ml. of 6 per cent. hydrogen peroxide amounted to 0·6 Lovibond red unit.

The 1 per cent. phloroglucinol solution in acetone keeps well in a dark-glass stoppered bottle. If it is kept in a clear-glass bottle, the solution gradually becomes yellow within a few days.

The original use of phloroglucinol in acetone and sulphuric acid is attributed by Bolton and Revis[7] to "Viedmann," but the original reference cannot be traced.

I wish to thank the Directors of Vitamins Limited for permission to publish this work.

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DISCUSSION

Mr. E. R. BOLTON hoped that the author, when referring to the fact that the substance which produced rancidity in fats was not the same in all fats, would not give the impression that the utility of the test might be limited to certain fats. He thought that most fats produced rancidity which fell within the limits of this test. Hence, the test should be distinctly useful and its quantitative application most valuable.

Mr. A. L. BACHARACH asked how permanent was the colour and whether it was necessary to fix any time limit for taking the reading? If the fat were extracted with ether, was it necessary to use peroxide-free ether, or were normal traces of peroxide not sufficient to interfere? Did the colour of the fat interfere with the colour obtained in the test?

Mr. D. FREELAND asked if the author had obtained any correlation with other tests, *e.g.* with the active oxygen test?

Mr. SAGE asked whether the author had found any difficulty with desiccated coconut. Occasionally he received samples which were not bad by the Kreis test, but, on tasting them, one would have no hesitation in saying that the coconut had begun to go rancid.

Mr. PYKE, replying, said that, broadly speaking, the active oxygen value and this test went together, but where laboratory experiments were devised, such as aeration, the correlation was not so good. He had found no difficulty in measuring the colour after fifteen minutes, even after running the solution through a dry filter. The presence of peroxide in the ether did not appear to make any difference. As regards the fat masking the colour, he had only done a few experiments with epihydrinaldehyde added to fats. He had not had any experience of desiccated coconut, but he had had cases of oil where it was difficult to apply the Kreis test, owing to the formation of emulsions or precipitates and where, by his method, solution could be obtained quite easily and the colour well matched.

A Counting-Field Finder

BY T. E. WALLIS, B.Sc., F.I.C.

(*Read at the Meeting, May* 1, 1935)

WHEN making counts of particles under the microscope, it is necessary to choose a number of fields in which the counts are to be made. The selected fields must be evenly distributed throughout the preparation, and any risk of counting the same field twice must be eliminated. To effect this purpose it is customary to use a mechanical stage and to place the centre of the mount under the objective; the position of the corner of the slide is then read off on the two scales of the stage, and the selected fields are brought successively into the centre by adjusting the mechanical movements. The necessity for using a special stage involves the analyst in additional expense and makes it impossible to carry out a series of counts with a microscope having a plain stage, a condition which also seriously hampers the introduction of quantitative determinations into ordinary class-work.

The finder described in this communication is designed to enable the analyst to use any microscope having a plain stage, and such a finder can be easily made by the microscopist himself to suit any selection of fields he may desire to use. The device consists of a piece of cardboard upon which is ruled a rectangle measuring 3 inches by 1 (*i.e.* the size of an ordinary microscope slide); above and below, and to the right and left of this rectangle lines are ruled at specified distances from the sides of the rectangle, the distances being marked by figures representing millimetres (see Fig. 1). A central opening, one inch in diameter, is cut in the card, which can be trimmed down to the size of the plain stage of the microscope and attached to it by any suitable means, such as by paper clips or by some adhesive.

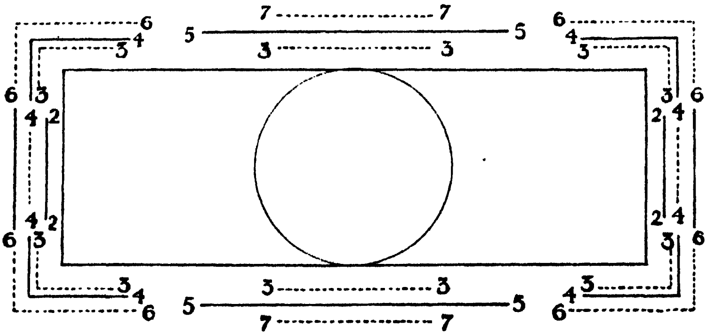


FIG. 1. Counting-field Finder. The arrangement represented corresponds to the selection of fields marked in Fig. 2.

The diagram (Fig. 2) represents the position of the fields to be examined in a microscopical mount, each field being indicated by its position in millimetres measured from two diameters intersecting at right angles, the particular fields represented being those which correspond to the rulings on the cardboard finder.

If a mount is now made centrally upon a slide and one wishes to examine the fields indicated, all that is necessary is to place the slide upon the finder so that its edges coincide with the rectangular outline and then move it successively to the right, to the left, above or below until its edge coincides with the line corresponding to the particular field to be examined. For example, to bring the field marked –6 into view, one would move the slide to the right until its right-hand edge coincides with the line marked 6 on the right-hand side of the card; similarly, if one wished to examine the field marked 4, 4, one would move the slide to the line marked 4 on the left-hand side, and to that marked 4 below the rectangle.

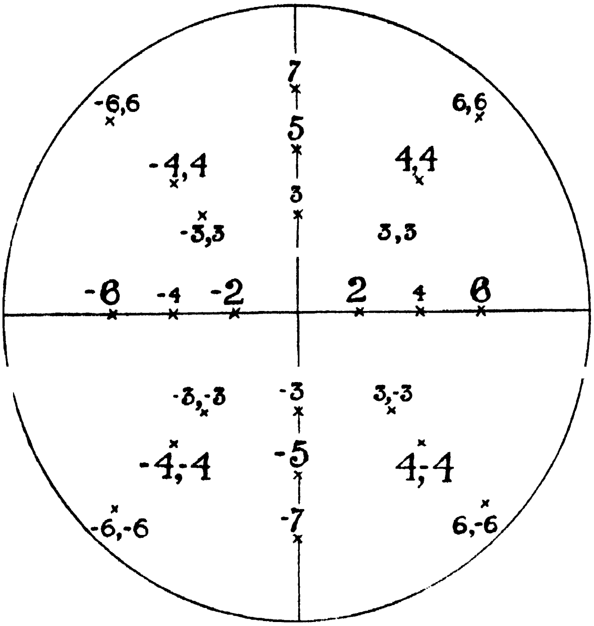


FIG. 2. Diagram to show the position of 10 selected fields, indicated by the larger figures, and of 15 other selected fields, indicated by the smaller figures and the centre of the circle. The figures in all cases represent distances in millimetres from the two intersecting axes.

Ten of the lines surrounding the rectangle are unbroken, whilst the remaining 14 are broken; this enables one to select 10 fields evenly distributed by moving the slide successively to the unbroken lines, or, in cases where a larger number of fields must be examined, one can increase the number to 25 by using the broken lines and also taking a count at the centre. If several of such cards are printed, a soiled card can quickly be replaced by a new one, and if some other distribution of fields is preferred, a similar finder can be drawn to suit the altered arrangement.

Micro-Volumetric Determination of Sulphur in Organic Compounds containing Halogen and Nitrogen

BY D. T. GIBSON, D.SC., AND T. H. CAULFIELD, B.SC., A.I.C.

COWIE and Gibson[1] showed that the combustion-volumetric determination of sulphur could be combined with that of chlorine, and the two elements satisfactorily determined by acidimetric followed by argentimetric titration.

Their process is greatly improved by the use of Vieböck's[2] mercuric oxycyanide for the halogen determination, which is resolved into an ordinary acidimetric titration with a sharp end-point.

At the same time we have taken the opportunity of introducing several other simplifications:—(i) The tube is maintained at a temperature of 400° C. electrically. (ii) The contact is a length of 80-mesh Pt/Rh gauze rolled into the form of a tube. (iii) There is affixed to the tube a 50-ml. distilling flask, the side-arm of which is bent bow-shaped, and has mid-way along its length a bulb blown.

Before attaching the flask, a boat containing about 8 mg. of sodium bicarbonate is introduced into it. The alkali is dissolved in 1 ml. of water, and 0·04 ml. of perhydrol is added. This solution is sucked up into the beads. The flask is then rotated so that the side-arm is in a horizontal position, and 0·04 ml. of perhydrol and 0·20 ml. of $N/100$ alkali are pipetted into the arm. This forms a seal which is broken intermittently by the oxygen flow.

After combustion, the products of oxidation are washed into the (receiving) flask, and the total acidity of the solution is found by titration with $N/100$ sulphuric acid.

The solution is now concentrated to 2 to 3 ml., 10 ml. of a saturated solution of mercuric oxycyanide are added, and the halogen-content is determined by titration with $N/100$ sulphuric acid, and hence by difference sulphur may be estimated.

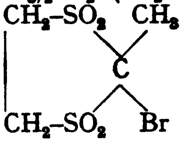
The equation

$$2\mathrm{Hg(OH)(CN)} + 2\mathrm{NaCl} \rightleftharpoons \mathrm{HgCl_2} + \mathrm{Hg(CN)_2} + 2\mathrm{NaOH}$$

represents the condition of the solution for the determination of halogen. In concentrated solution equilibrium lies practically quantitatively to the right, and the sodium hydroxide may be titrated with acid other than halogen acid. Dilution of the solution shifts the equilibrium to the left, and it is therefore necessary to arrange conditions so that the acid does not add unduly to the dilution, or results will be low.

With bromides the degree of accuracy is equally good.

Compound	Sulphur found Per Cent.	Sulphur required Per Cent.	Chlorine found Per Cent.	Chlorine required Per Cent.
Dichlorobenzene, $C_6H_4Cl_2$			48·3, 48·4	48·3
Tetrachlorodiphenyl disulphoxide, $C_{12}H_6O_2S_2Cl_4$	16·5	16·5	36·7	36·5
Chlorophenylsulphonacetone, $C_9H_9O_3SCl$ ..	13·6	13·5	15·3	15·1
Ethyl chlorocamphorsulphonate, $C_{12}H_{18}O_3SCl$	11·4	11·5	12·5	12·1
Dichlorophenylsulphone, $C_{12}H_8O_2SCl_2$ ..	11·1	11·3	25·2	25·1
Tetrachlorodiphenyl disulphide, $C_{12}H_6S_2Cl_4$ ..	17·7	17·9	39·4	39·9
Naphthalene sulphonchloride, $C_{10}H_7O_2SCl$ ..	14·0	14·2	15·8	15·7
Toluenesulphonchloride, $C_7H_7O_2SCl$	16·4	16·8	18·5	18·1

Compound	Sulphur found Per Cent.	Sulphur required Per Cent.	Bromine found Per Cent.	Bromine required Per Cent.
Ethyl bromocamphorsulphonate, $C_{12}H_{18}O_3SBr$	9·69	9·94	24·6	24·8
Bromophenylmethylsulphone, $C_7H_7O_2SBr$ ..	13·9	13·6	34·0	34·0
$CH_3OC(CH_3)_2SO_2C(SO_2Me)Br_2$	16·2	16·5	40·8	41·2
	24·0	24·4	29·9	30·4
Tolyldibromopropylsulphone, $C_{10}H_{12}O_2SBr_2$	9·28	9·00	45·8	45·0

For compounds containing nitrogen, Friedrich[3] has proposed a volumetric method for determining sulphuric acid; it is based on the stability of potassium bisulphate.

We have applied this to artificial mixtures of nitric and sulphuric acids, with the following results:

Nitric acid (0·0170 *N*) ml.	Sulphuric acid (0·00912 *N*) ml.	Sodium sulphate (0·0210 *N*) ml.	Alkali found (0·0113 *N*) ml.	Alkali required (0·0113 *N*) ml.
1·00	3·00	5·00	2·49	2·48
3·00	3·00	5·00	2·50	2·48
1·00	3·00	6·00	2·50	2·48
3·00	3·00	6·00	2·50	2·48
2·00	3·00	8·00	2·50	2·48
5·00	3·00	6·00	2·50	2·48
—	3·00	10·00	2·50	2·48

When the method was applied to products of combustion of compounds containing sulphur, the results were always 1 to 3 per cent. low. For example, the following results were obtained with propylene diphenylsulphone ($C_{15}H_{16}O_4S_2$):

Sulphur (direct titration)	Sulphur (after Friedrich)		Sulphur (required)
Per Cent.	Per Cent.	Per Cent.	Per Cent.
19·6	18·6	18·4	19·8
	17·9	17·0	

As the discrepancy was probably due to incomplete conversion of $SO_2 \rightarrow SO_3$ by perhydrol, chlorine water was substituted. Here the results were variable, sometimes tending to be high, owing to retention of hydrochloric acid (as indicated by silver nitrate), which caused us to reject the method.

Compound	Sulphur found Per Cent.	Sulphur required Per Cent.
Propylenediphenylsulphone	19·7	19·8
Toluenesulphonamide	18·6	18·7
Thiourea	42·3	42·1
Dinitrodiphenyl disulphide	20·0	20·8
4-Chloro-3-nitro-4′-2′ dinitrodiphenylsulphone	6·25	8·21
Nitrodiphenyl sulphide	15·7, 13·4	13·8

Other methods tried and subsequently discarded (for reasons indicated in parenthesis) included potassium palmitate [(Halm, Vieweg and Meyer),[4] (variable *p*H)]; rhodizonic acid [(Strebinger and Von Zombory[5]) (satisfactory for *N*/10 solution, not for *N*/100)]; tetrahydroxyquinone [(Schroeder[6]) (for the same reasons as rhodizonic acid)]; and benzidene [(Muer)[7] (occlusion, giving high results)].

A method based on the use of barium chloride and potassium chromate was found to be a distinct improvement on others, and was finally adopted.

Compound	Sulphur found Per Cent.	Sulphur required Per Cent.
Propylenediphenylsulphone, $C_{15}H_{16}O_4S_2$	19·5	19·8
Camphor sulphonylmethylsulphonylmethane, $C_{12}H_{20}O_4S_2$ ..	21·2	20·8
Benzyl sulphonylmethylsulphonylmethane, $C_9H_{12}O_4S_2$ ..	25·7	25·9
Thiourea, CH_4SN_2	42·8	42·1
,, ,, ...	42·3	42·1
Dinitrodiphenyl disulphide, $C_{12}H_8O_4S_2N_2$	20·6	20·8
Toluenesulphonamide, $C_7H_9O_2SN$	18·4	18·7
Cystine, $C_6H_{12}O_4S_2N_2$	26·6	26·7
Nitrodiphenyl sulphide, $C_{12}H_9O_2SN$	13·8	13·8
Sulphanilic acid, $C_6H_7O_3SN$	18·5	18·5
Thiocarbanilide, $C_{13}H_{12}SN_2$	14·1	13·9
Phenyl-sulphonyl-acetonitrile, $C_8H_7O_2SN$	17·4	17·7
,, ,, ,, ,, ...	17·5	17·7
4-Chloro-3-nitro, 2′-nitro-4′-nitro-diphenylsulphone, $C_{12}H_6O_8SN_3Cl$	8·25	8·25
4-Bromo-3-nitro-2′-nitro-4′-nitrodiphenylsulphone, $C_{12}H_6O_8SN_3Br$	7·27	7·41
4-Chloro-2′-nitro-4′-nitro-diphenylsulphone, $C_{12}H_7O_6SN_2Cl$ ..	9·11	9·37

The combustion of the compound was carried out in an ordinary Pregl tube heated to 400° C. The improved Pt/Rh contact was used. A pre-catalyst of platinum foil was also employed. This was heated to a temperature between 500° to 600° C., to promote the disruption of the compound. The beads were moistened with distilled water only. The products of combustion were washed into a receiver and neutralised with *N*/100 alkali. The sulphate was precipitated in hot neutral solution by drop-wise addition of barium chloride solution (*N*/100).

The excess of barium chloride was precipitated with potassium chromate solution, and the combined sulphate and chromate precipitates were filtered off and washed on an Emich filter-stick. The filter-stick was then washed and boiled in dilute hydrochloric acid solution. The solution was cooled, potassium iodide was added and the liberated iodine was titrated with $N/100$ thiosulphate solution. The determination can be complete in less than 2 hours.

The preliminary alkali titration varies, but it gives an upper limit to the acidity of the solution, and hence a measure of the volume of barium chloride solution required.

The excess of the total acidity over the sulphur acidity varies by from 5 to 20 per cent. of the latter for the sulphur-nitrogen-compounds analysed, whilst for the sulphur-nitrogen-halogen-compounds it rises to over 100 per cent.

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The Liver Oil of Norway Haddock
(Sebastes marinus)

BY T. THORBJARNARSON

WITHIN the last few years considerable interest has been shown in fish-liver oils of high vitamin-content. Halibut-liver oil is probably the best known representative of these oils, although several others, among them tunny-liver oil, have been investigated as promising sources of vitamin *A* and vitamin *D*. Investigations made by me a few months ago indicated that the liver oil of *Sebastes marinus* might also be of value in this respect.

So far as I am aware, the literature contains no information concerning the composition of this oil, so that, apart from the question of vitamin-content, an investigation of its characteristics appeared desirable.

The occurrence of *Sebastes marinus* is limited to the Arctic Ocean and the North Atlantic. It is found off the coasts of Iceland, Greenland, Norway, North America and Scotland, usually at considerable depths. It is particularly plentiful in the cold waters of the more northerly of these countries.

The length of *Sebastes marinus*, as caught for food, is usually about 30 cm., but sometimes it may measure as much as 100 cm. Its height is about two-sevenths of its length and its width about two-thirds of its height. The head is large and high with large eyes and a protruding lower jaw. The body is short, only a little longer than the head, with a short tail. It has only one rather long dorsal fin and one ventral fin. The scales are large and rather irregularly placed. The colour is dark red on the back, and lighter red or almost white on the belly.*

It is commonly known in England as "Norway Haddock," "Soldier" or "Berggilt." The usual mode of catching is by trawl or on a long line.

Sebastes marinus is an excellent food fish and is used extensively as such in Germany. A related fish is *Sebastes viviparus*. Both species are of interest in being viviparous.

One oil employed for this investigation was obtained from the livers of some 50 fish caught off the coast of Iceland in the middle of September, 1934. The livers amounted to 1·5 per cent. of the weight of the fish, but although they contained 30 per cent. of oil, only one-third of it was liberated when the livers were subjected to treatment with live steam; halibut livers behave similarly under steam-treatment. Haines and Drummond (unpublished data), studying this behaviour, have found that it is related to the structure of the liver tissue. A relatively high proportion of connective and fibrous tissue in certain livers (*e.g.* the halibut) tends to prevent complete resolution of the liver substances during steaming, and consequently more oil is retained by the mass of coagulated protein. Sometimes the occlusion is almost complete.

The values obtained in the examination of this sample of the liver oil (A) are given below. For comparison, some data regarding another sample of oil (B), obtained from an industrial source, are also given.

LIVER OIL OF *SEBASTES MARINUS*

	A	B
Saponification value	180·0	180·7
Iodine value	170	133
Refractive index, n_D^{18}	1·4820	n_D^{40} 1·4693
Sp.gr. at 18° C.	0·9238	—
Unsaponifiable matter, per cent.	3·95	4·55
$SbCl_3$ test "Blue value" (B.P. method)	895	180
$E_{1\,cm.}^{1\%}$	18·4	—
Vitamin *A*, per cent. (based on spectroscopic assay) ..	1·14	—
Iodine value of unsaponifiable matter	178	140
"Blue value" of unsaponifiable matter	23,260	—
$E_{1\,cm.}^{1\%}$ of unsaponifiable matter	475	—
Vitamin *A*, per cent. on unsaponifiable matter (based on spectroscopic assay)	29·6	—

It will be noticed that the oil differs in several respects from halibut-liver oil. For example, the iodine value of sample A is considerably higher than any of those recorded by Haines and Drummond (*Brit. Med. J.*, 1933, April 1) for halibut-liver oil. On the other hand, it contains a smaller proportion of unsaponifiable matter.

EXAMINATION OF THE UNSAPONIFIABLE MATTER.—In view of the high value obtained for the vitamin *A*-content of the unsaponifiable of oil A, it was thought that a fractional adsorption by means of aluminium oxide might effect a concentration of that substance, and at the same time throw some light on the character of the other substances present. The experiment was carried out on

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* A full description of this fish is given in a reference work on Icelandic fish, "Fiskarnir," by Professor Bjarni Saemundsson, Reykjavik, 1926.

2·14 g. of the unsaponifiable matter dissolved in a mixture of light petroleum and benzene (75 to 25). The procedure of the adsorption was similar to that described recently (Thorbjarnarson, Santos-Ruiz and Drummond, ANALYST, 1935, 382).

2·14 G. OF UNSAPONIFIABLE MATTER ADSORBED

	Weight g.	Vitamin *A* Per Cent.
Original unsaponifiable matter	2·14	29·6
Fraction I filtrate (material not adsorbed)	0·03	0·16
Fraction II, bottom zone from column (least adsorbed)	0·04	0·6
Fraction III, 2nd zone from bottom of column ..	0·30	17·4
Fraction IV, 3rd zone from bottom of column ..	1·28	
sterol	0·69	65·8
non-sterol	0·59	(sterol-free fraction)
Fraction V, top zone of column (most adsorbed) ..	0·14	12·0

Practically all the sterols were found in Fraction IV, together with most of the vitamin *A*. This material was fractionally crystallised from methyl alcohol at 0° C. Several fractions of sterol (m.p. 148° C.), fully identified as cholesterol, were obtained. The mother liquors from the sterol fractions were concentrated and taken down to dryness *in vacuo*. More than 0·5 g. of an oily material consisting of over 60 per cent. of vitamin *A* was obtained. This represents a very effective concentration of the vitamin *A* by a single adsorption.

Fractions I, II and III were too small to investigate thoroughly, but appeared to consist mainly of cholesterol and a small amount of vitamin.

In order more fully to investigate the nature of the other substances present in the unsaponifiable fraction a larger amount was prepared from the commercial oil B. Of the 34 g. of material obtained, approximately 20 g. were removed, by crystallisation from methyl alcohol at 0° C., in the form of a number of fractions consisting almost entirely of cholesterol. The residual material was a heavy yellow oil, and approximately 14 g. were subjected to fractional adsorption on aluminium oxide, as previously described.

The material which passed through the column without being adsorbed weighed 0·218 g. and had an iodine value of 114. On treatment of a small sample in dry acetone with hydrochloric acid gas, typical crystals of squalene hydrochloride were obtained. Without further purification they melted between 116 and 120° C.; the yield suggested that the greater part of the unsaturation represented by the iodine value of the fraction was due to squalene. This indicated that the substance other than squalene might be a liquid saturated hydrocarbon, but the amount available was too small for further investigation.

The material adsorbed in the column showed a distribution resembling in general character that described for the previous experiment. There was a similar concentration of the vitamin *A*, although much less was present than in oil A. All the fractions consisted largely of cholesterol; the substances accompanying it appeared to be vitamin *A* and a liquid unsaturated alcohol of a similar type, resistant to hydrogenation at room temperature over platinum or palladium catalysts; this was not satisfactorily separated.

These experimental results seem to indicate that the unsaponifiable fraction of the liver oil of *Sebastes marinus* consists mainly of cholesterol and vitamin *A*, together with small amounts of squalene, an unsaturated alcohol possibly related to vitamin *A*, and possibly a saturated hydrocarbon. No evidence was obtained of the presence of oleyl, selachyl, chimyl or batyl alcohol, so often found in fish-liver oils from other sources.

VITAMIN *A* CONTENT.—A considerable number of samples of this liver oil have been examined for vitamin *A* content; in most cases the antimony trichloride reaction was employed. The oils showed wide variations in the amount of vitamin *A* found present, as the following figures will show:

Blue value (B.P. method)	No. of oils examined
1–100	14
100–200	6
200–300	7
300–400	2
400–500	2
500–600	1
600–700	1
700–800	6
800–900	2
900–1000	2
1000–1500	2
1500–2000	3
2000–2500	1
2500–3500	1

It is highly probable that these variations can be correlated, as in the case of other fish-liver oils, with the age and sex of the fish, its physiological condition, and the nature of its food supply. Unfortunately, the relevant information for these samples is not available.

DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY COLLEGE, LONDON

A Method for the Quantitative Determination of Mechanical Wood Pulp, Unbleached Chemical Pulp, and Bleached Chemical Pulp Fibres in Paper and Pulp

By B. K. MUKHOPADHYAY, M.Sc., and K. K. TAMPY, M.A.

The quantitative determination of mechanical wood pulp, bleached chemical pulp and unbleached chemical pulp, when all the three are present together, as in cheap newspaper and wrapping papers, has not been satisfactorily worked out, and the present work was undertaken to devise a method. It was found that by combining the results of counts carried out as in Cross and Bevan's method, using the two stains separately, a formula can be worked out which gives the percentage of the three classes of fibres. The method gave results which were found to be quite within the limits of experimental error in fibre-count methods of analysis.

Outline of the Method.—A sample taken from paper (or pulp) containing mechanical wood pulp, unbleached chemical pulp and bleached chemical pulp, freed from sizing, fillers, etc., is thoroughly disintegrated by shaking with water and a few drops of the suspension are transferred by means of a glass tube to a number of microscope slides. The slides are divided into two batches. Those of one set are stained with Herzberg's solution, which stains mechanical wood pulp fibres yellow, and the chemical pulp fibres pink. The remaining slides are stained with Cross and Bevan's ferric ferricyanide solution, which stains the mechanical wood pulp and unbleached chemical pulp fibres deep green and blue, leaving the bleached chemical pulp fibres colourless. The lengths of the yellow and pink fibres are separately counted in the first set, and those of the coloured and uncoloured fibres in the second set of slides. Applying Spence and Krauss' weight factor (0·55) to the length of chemical pulp fibres, the relative percentages of the three classes of fibres may be calculated.

Calculation.—Let a and b be the respective lengths of yellow and pink fibres, as obtained on counting the first set of slides.

Let x and y be the respective lengths of coloured and uncoloured fibres, as obtained on counting the second set of slides.

Then, the ratio of the lengths of mechanical wood pulp fibres to the total length is as

$$\frac{a}{a+b}$$

So that, in the second count, the relative lengths of mechanical wood pulp fibres

$$= (x+y)x\frac{a}{a+b} \qquad \cdots \qquad \cdots \qquad \cdots \qquad \text{(i)}$$

Hence, the lengths of unbleached fibres

$$= x - (x + y)x \frac{a}{a + b} \quad \ldots \quad \ldots \quad \ldots \quad \text{(ii)}$$

and the lengths of bleached fibres $= y$ .. .. (iii)

Then, by applying the weight factor 0·55 to (ii) and (iii) and calculating, the respective percentages of mechanical wood pulp, unbleached chemical pulp and bleached chemical pulp fibres can be determined.

PROCEDURE.—A few pieces are punched out from different parts of the paper by means of a round punch of ¼-inch bore. The pieces are boiled with 1 per cent. sodium hydroxide solution in a beaker for two minutes, and the liquid is drained off. The pulp is washed twice with distilled water, the washings being drained off each time. It is then washed with 1 per cent. hydrochloric acid, followed by another washing with distilled water.

The treated pulp is kneaded to loosen the fibres, after which it is transferred to a 100-ml. stoppered cylinder, together with a dozen glass beads or lead shots. About 70 ml. of distilled water are added, and the pulp is shaken until the fibres separate out and no clusters are visible.

A portion of the pulp is taken out of the suspension by introducing a glass tube, of 6 mm. bore, into it to a depth of 2 inches, transferred to a microscope slide, and heated on an air-oven or hot plate until just dry. The slide is then cooled and the pulp stained with Herzberg's solution.*

The two solutions are mixed just before use, and two drops are placed on the slide containing the dried pulp. The liquid is allowed to moisten every portion of the pulp. A cover-glass is then placed on top and pressed gently into position, the excess of solution being removed by means of blotting paper.

The slide is placed under a microscope fitted with a travelling stage and a micrometer eyepiece divided into 10/10 mm. squares and examined at various positions. If more than four complete diameter-lengths appear in any field, the original suspension should be suitably diluted and fresh slides made up for counting.

Six such slides are made and dried. Three slides are stained by the process described above, and the fibres are counted under the microscope. Lengths only of each of the differently stained fibres are counted, in terms of the side of one of the small squares of the micrometer, taken as unit. The whole slide is gradually counted by moving the travelling stage in each direction. The results are recorded, *e.g.* as follows:

Yellow: 23 + 13 + 25 + 40 + 20 + 47 + 21 + 17 +
35 + 48 + 35 + 12 + 38 + 17 = 391

Pink: 25 + 25 + 39 + 30 + 15 + 27 + 20 + 39 +
40 + 17 + 23 + 17 + 12 + 12 + 28 + 10 = 379

The remaining three slides are stained with Cross and Bevan's ferricyanide stain (*cf. Allen's Organic Analysis*, 5th Ed., Vol. I, pp. 599–600). Twenty ml.

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* This consists of 2 parts:—
(A) 20 g. of zinc chloride dissolved in 10 ml. of water.
and (B) 2·1 g. of potassium iodide and 0·1 g. of iodine dissolved in 5 ml. of water.

each of the ferric chloride and potassium ferricyanide solutions of Cross and Bevan's stain are placed in a tall beaker and mixed, and the covered beaker is allowed to stand at 32° to 35° C. The prepared slides are immersed in water until the fibres are uniformly wet, care being taken to avoid air bubbles. The wet slides are then placed in the mixed ferric chloride and potassium ferricyanide solutions at 32° to 35° C., and left for 15 minutes, after which they are taken out, one by one, and washed up by being dipped 6 times in and out of a beaker containing distilled water, followed by a similar rinsing in another beaker containing a fresh quantity of water. Cover-slips are now put on, and the fibres are counted under the microscope (lengths only) as usual.

The lengths of the coloured fibres are counted, together and those of the uncoloured ones, separately, and the mean of the counts is taken. The results are tabulated as "Coloured" and "Uncoloured," as described on p. 529.

In an experimental determination the number of lengths of (i) mechanical wood pulp; (ii) unbleached chemical pulp; and (iii) bleached chemical pulp were 203·6, 101·4 and 96, respectively, and by multiplying (ii) and (iii) by 0·55, the relative weights of the respective fibres were obtained; from these the percentages were calculated as 65·3 of (i), 17·9 of (ii), and 16·8 of (iii).

Some made-up mixtures of mechanical wood pulp, unbleached sulphite pulp and bleached sulphite pulp gave the following figures:

Mechanical wood pulp		Unbleached chemical pulp		Bleached chemical pulp	
Present Per Cent.	Found Per Cent.	Present Per Cent.	Found Per cent.	Present Per Cent.	Found Per Cent.
64	65·3	20	17·9	16	16·8
70	71·4	25	24·4	5	4·2
70	71·0	20	19·9	10	9·2

The results obtained lie within the limits of experimental error in fibre-count methods of analysis. The stains taken are so striking, that there is little chance of mistaking one class of fibres for another. The only precautions necessary are to prevent dust settling on the ferricyanide stain and to avoid air-bubbles when the slides are being wetted preliminary to being put into the staining solution.

If preferred, the substantive red stain described by Bright (*cf.* Allen, *loc. cit.*, pp. 599–600) may be used over the ferric ferricyanide stain in the second set of slides, but this is not essential.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF COPPER IN FOODS

In connection with the paper by Lampitt and Sylvester on "The Determination of Copper in Foods, with special reference to Milk" (Analyst, 1935, 376), an observation made in this laboratory may be of interest. Shortly after the publication of a method for the determination of minute amounts of copper by Haddock and Evers (Analyst, 1932, **57**, 495) we carried out a number of tests to find how the method could best be adapted to our particular purpose, which involved the analysis of organic solids and solutions containing phosphates. The organic matter was removed by ashing in silica dishes with a small amount of sulphuric acid in a manner similar to that described by Lampitt and Sylvester, the ash being then dissolved in hydrochloric acid and the phosphates kept in alkaline solution by the addition of ammonium citrate. On carrying out analyses with known amounts of added copper (0·01 to 0·05 mg.) we discovered that there was a small, variable loss of copper at some stage, which was traced to the ashing process. The loss did not appear to be related to temperature (over a range of about 400° to 700° C.), but it was noticed that when the ash was small and came into close contact with the silica, the loss was greater than with a bulky ash. The substitution of magnesium nitrate as an ashing agent in place of sulphuric acid was accordingly tried, and the non-adherent, bulky ash so obtained was removed from the silica dish to a Pyrex glass flask before being dissolved in the hydrochloric acid, which was first used to "extract" the emptied silica dish. Additional ammonium citrate was, of course, needed to keep the magnesium phosphate in alkaline solution. With these precautions all the added copper was recovered.

From ashes made with sulphuric acid, part, but never the whole, of the missing copper was recovered by repeated extraction of the silica dish with hydrochloric acid. The dishes used for these tests were old, with the inner surfaces somewhat corroded, and it was found that when new silica dishes with their smooth glazed surfaces were used, the sulphuric acid ashing process suffered either a very much smaller loss of copper or none at all. It would appear that in some states silica has a tendency to absorb copper, and that copper so absorbed is very difficult to recover.

By using magnesium nitrate and dissolving the ash out of contact with silica, the method has given satisfactory results for the past two years.

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A MODIFIED PROCEDURE FOR THE DETECTION OF NITRATES IN MILK

The development of the qualitative test for the detection of nitrates in milk, a positive reaction confirming the evidence of the presence of added water, is summarised by Lerrigo (Analyst, 1930, **55**, 435). Monier-Williams (Analyst, 1931, **56**, 397) has made the test more sensitive by the introduction of the intermediate diphenylbenzidine instead of diphenylamine as the reagent.

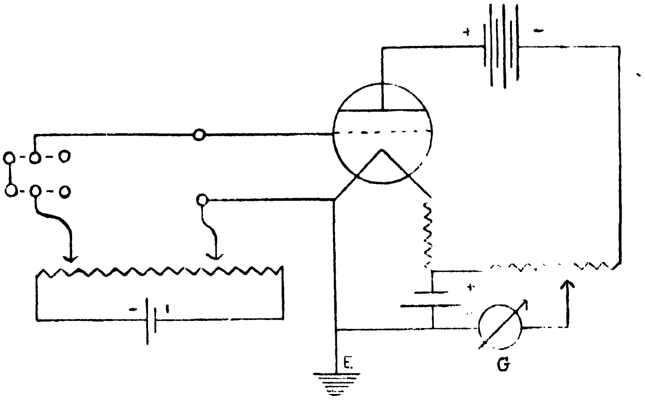

Fig. 1.

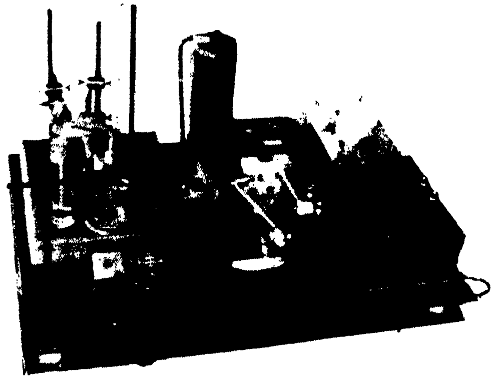

Fig. 2.
Modified glass electrode

The test depends upon the formation of a blue ring between the reagent and the milk serum, and is carried out in a test-tube. By performing the test in a capillary tube instead of a test-tube the greater part of the contents of the capillary tube turns blue when nitrates are present. This mode of procedure has been found to possess several advantages over the test-tube method.

Procedure.—Capillary tubes of internal diameter between 1·0 and 1·5 mm. in diameter and 10 cm. in length are prepared by washing a piece of glass tubing, inside and out with hot water, and drawing it out in the blow-pipe flame. The diphenylbenzidine reagent is drawn into the tube, either by capillary action or by means of a small rubber bulb attached to the upper end, to a distance of 6 cm. The clear milk serum, which is prepared according to the method of Lerrigo (*loc. cit.*), is then drawn into the reagent until the combined serum and reagent fill the tube to within 2 cm. of the top. The tube is then wiped with a piece of filter-paper and placed on a white tile; the tube is observed at the end of 15 minutes. When nitrates are present a blue colour develops in about ¾ of the length of the tube, and the intensity of the blue colour is proportional to the amount of nitrate present.

By this method it has been found that the presence of traces of nitrates is detectable with far greater precision than is possible by the test-tube method. A genuine milk, to which 2 per cent. of London tap water has been added, will give a definite blue colour when tested in this manner. It is also possible in this way to compare the intensity of the blue colour given by a milk with that given by a genuine milk to which a known amount of nitrate has been added.

For this test it is not necessary that the solution of diphenylbenzidine in sulphuric acid should be perfectly colourless, since a slight blue colour of the reagent is not detectable in the thin column of liquid that is viewed in the tube. This is an advantage, since it is sometimes a matter of considerable difficulty to obtain a sample of sulphuric acid that will give a colourless solution with diphenylbenzidine. The risk of atmospheric contamination and the possibility of erroneous results due to traces of foreign matter in test-tubes are largely diminished in the capillary method.

Formaldehyde.—It is stated in the literature (Lerrigo, *loc. cit.*) that formaldehyde is one of the compounds which produce a blue colour with diphenylamine, but it has been found that genuine milks to which traces of formaldehyde have been added, in order to preserve the samples, do not yield a blue colour when examined in this way.

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NOTES ON THE TECHNIQUE OF THE GLASS ELECTRODE

The determination of the acidity of gallo-tannate iron writing inks, both as to intensity and proportion, regularly required in this laboratory, necessitates the employment of electrometric methods of measurement. Of these, the quinhydrone and hydrogen electrode systems are of doubtful value, owing to the complex and peculiar composition of the test materials, and recourse must therefore be had to the glass electrode, which has been ascertained to give satisfactory results if certain precautions are observed.

We have used a modification of the circuit of Harrison illustrated in Fig. 1, employing the Electrometer T valve of the G.E.C. The characteristics of this valve are such that extreme thinness of the glass electrode membrane is unnecessary, so that the risk of accidental damage and of porosity are much reduced. We have had experience only of the Morton type of electrode of which the shape is very convenient for the particular work. An electrode is standardised on each occasion before use against standard buffer solutions at no fewer than three positions on the Nernst curve. Variation from the theoretical values of an order of 4 to 6 m.v., after making allowance for parallel displacement due to the natural unbalance of the particular components of the "gas chain" used in the circuit, is commonly attributed to an "asymmetry potential" on the glass itself. An electrode with really good characteristics appears to be something of a rarity. We have not found it necessary to steam the glass, but its exterior should be kept in contact with distilled water of as nearly neutral reaction as possible; or, alternatively, when routine determinations are to be undertaken in a restricted region, in a buffer solution corresponding with a figure in that region. Our practice is to keep the bulb filled with *N*/2 hydrochloric acid used in conjunction with the silver-silver chloride system of McInnes and Dole. This system eliminates the inevitable contact potential introduced by a second calomel half-cell, but there appears to be no objection to the substitution of quinhydrone in conjunction with platinum.

To prevent, as far as possible, diffusion and hydrostatic effects, we have found it desirable to introduce a special potassium chloride bridge intermediate between the test solution and the single calomel half-cell. This bridge is in the form of a glass U-tube inverted, containing a length of pure white cotton cord previously well bleached in hypochlorite and thereafter thoroughly washed and kept continuously in contact with saturated potassium chloride solution. A piece of this cord trails for a fair proportion of its length in a beaker of saturated potassium chloride solution, whilst its other end dips for a short distance into the test solution (Fig. 2). At each change of test the short contaminated portion is cut off, and a fresh portion is exposed. The arrangement appears to work well and gives less trouble than the orthodox bridge. The test-beaker is continuously rotated at the rate of 78 r.p.m. by means of a Simpson synchronous A.C. turntable, supporting a small circular platform moulded in "halowax," upon which the beaker rests. At first we arranged the glass electrode to fall excentrically into position in the beaker in order that it should act as an efficient stirrer, but this arrangement was found to give rise to a rhythmical vibration of the galvanometer needle, and has been abandoned. A sufficient stirring movement appears to result from the trailing cord of the bridge. Potentials in a still liquid may differ by several millivolts from those given under conditions of agitation, while the lag in attainment of equilibrium when an electrode is moved from one test to another appears to be shortened by stirring. Stirring is needed, of course, in any case for titrations.

Much trouble was originally experienced from induction into the D.C. circuit from the A.C. mains and motor stator winding, the galvanometer zero undergoing erratic displacement when making or breaking the A.C. line, and acquiring a permanent set upwards on the scale; but this trouble has been completely prevented by the process of shunting a 2 m.f. high test condenser across the mains in conjunction with earthing of the motor casing.

With reasonable care the circuit appears to be nearly immune from capacity influences, and, with the exception of the valve and its grid connections throughout, no parts are, as a rule, specially shielded. Grid leads are everywhere taken through glass tubing filled with "halowax" and jacketed with earthed copper wire in spirals. The valve is mounted in three sockets supported in "halowax," while, as a counsel of perfection, its anode leg-socket is detached and air-insulated. A light copper box, with doors at the top, is available for surrounding the electrode and its lay-out complete, fitting round the thick "halowax" block on which these are supported, with provision for admitting the end of the cranked burette used during titrations, and this box is earthed when in use by means of a flexible copper lead. The valve is housed in a light-tight copper cylinder having a "halowax" plug fitted round its grid terminal.

Experience has shown that no precautions possible to be taken against electrical leakage may be omitted. In every instance where insulation is necessary and cannot be contrived by air-mounting, a chloro-naphthalene wax has been used. All switch-gear is moulded and carved out of this material, and all necessary terminals and pillars are mounted thereon, as is also the potentiometer (2 Fig. 1a). Wherever possible, connections are made by little pools of mercury contained in drill-holes in the wax. The glass body of the valve, the stem of the Morton electrode, and the silver wire fitted therein, are all waxed, the two ends of the wire, of course, being left bare, while the test terminals of the main potentiometer (Gambrell) are air-insulated. The use of ebonite, or even glass, has been found fatal to consistent and satisfactory results. A controlled humidity in the vicinity of the apparatus is desirable, though not absolutely essential, and every precaution must be taken to exclude dust, the presence of which may necessitate periodical scraping of the wax surfaces.

The current required by the valve filament (approximately 100 m.a.) is maintained correctly by a rheostat in series with a milliammeter, the reading of the latter having been ascertained once and for all for a potential of one volt exactly upon the filament. The main potentiometer coils—of aged manganin—must be of adequate current-carrying capacity and calibrated to an accuracy of not less than ±0·05 per cent. Allowance must be made for thermo-electric effects at junctions. The small potentiometer is a high class wireless instrument (Varley type CP64).* The Cambridge Unipivot galvanometer, used as a null-point indicator, has been found to give trouble from electrostatic disturbance due to friction on the glass, but any such difficulty is easily controlled in the manner described in the reference (*Nature*, **133**, 948). By an arrangement of cross-connections we employ the same instrument, which is fitted with the necessary winding, for the determination of the standard volt. This system may be open to criticism, but in practice it is found possible to read to close limits of accuracy, while it has the advantage of dispensing with the somewhat costly certificated cadmium cell otherwise required. Zero points are read with the aid of a small microscope having cross-wires in its eyepiece-field. The aluminium case of the instrument is earthed. The change over from standardisation of the volt to the "test" may be made, for all practical purposes, without the use of a compensating resistance, the error thus introduced into final computations being negligible with the instrument in question.

In our experience a stable zero corresponding to a balance of the system obtained with a grid bias potential on the valve of the order of about minus 1·2 volts is rarely obtainable under one to two hours, and readings on test solutions are not taken until the expiration of this period of time. Battery voltage drift is an ever-present possibility. I am indebted to Mr. C. Morton for advice leading to the adoption of cells of starter battery capacity, and these cells require every care in upkeep. The anode battery, however, with a constant discharge of only a few microampères may be a wireless instrument. It appears theoretically possible to use A.C. mains in place of accumulators, the various circuits being driven from separate secondary windings on a common transformer through Westinghouse rectifiers, but so far we have not attempted this. Adequate smoothing might cause difficulties. We have occasionally noticed a shift of zero (reference) potential of a somewhat perplexing nature when changing test solutions, but such shift is usually small and nearly always cancelled out by a corresponding change in the e.m.f. of the test itself. Of four consecutive potential determinations agreeing to one or two millivolts, the last is taken as the true figure.

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* It can be shown mathematically that for the sensitivity of the circuit to be a maximum it is necessary to keep R3 and R1 (Fig. 1) as small as possible. Apart from consideration of the galvanometer itself, this may be effected by using a value for the potentiometer of not more than 20,000–25,000 w. in conjunction with an anode potential on the valve of about 6 to 8 volts to enhance its mutual conductance.

For the determination to close limits of accuracy of the actual amount of mineral acid present in a gallo-tannate iron writing ink a titration with $N/4$ sodium hydroxide solution under the conditions to be described is practicable with this apparatus. The most satisfactory form of burette is one of 10-ml. capacity, with a narrow bore graduated to 0·05 ml., and having a cranked exit tube, so that it can be supported at a little distance from the test-beaker. In order to ascertain a satisfactory working-point on which to base "neutrality," a number of determinations has been made to find the *p*H of a normal ink (iron, 0·25 per cent.; ratio of ferrous sulphate to tannin = 1 : 3·8), to which no mineral acid has been added. Immediately after union of the reagents the *p*H referred to has been shown to be approximately 2·9, this figure becoming progressively lower with time, until, after the expiration of 24 hours, it is stable at about 2·5. At this stage there is evident a degree of precipitation which would render an unacidified ink useless. The falling value appears to be a function of the more complete dissociation of the oxidation products formed, but equilibrium is nevertheless apparently attained within the time mentioned. The early addition of mineral acid (for preference sulphuric) facilitates equilibrium, and the point of "neutrality" of a freshly manufactured ink is therefore reasonably to be taken at *p*H 2·9. This end-point being once decided on, it is only necessary when standardising to determine the variation from the theoretical of the e.m.f. given by the standard buffer solution corresponding to the said end-point. If the potentiometer be adjusted to the equivalent potential, with allowance for any electrode eccentricity, the end-point (as shown by the galvanometer needle) is abrupt and sensitive to one drop of alkali.

The total cost of the apparatus, including batteries, as constructed entirely in this laboratory, does not exceed £25, which compares very favourably with that of the best commercial outfit available.

I acknowledge much indebtedness to the scientific staff of Messrs. D. Gestetner, Ltd., for assistance and advice, which have materially contributed to successful results.

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Erratum:

A MODIFICATION of Thorpe and Holmes's Method for the Determination of the Total Proportions of Methyl, Ethyl, *Iso*-propyl and Propyl Alcohols. By S. S. Aiyar and P. S. Krishnan. April issue, p. 239. In the last line of Table II, *for* "6 × 6 ml. H_2O wash" *read* "6 × 10 ml. wash."

Report of the Sub-Committee on the Determination of Unsaponifiable Matter in Oils and Fats and of Unsaponified Fat in Soaps to the Analytical Methods Committee of the Society of Public Analysts

REPORT No. 2

THE DETERMINATION OF UNSAPONIFIED FAT IN SOAPS

AT the conclusion of the inquiry into the determination of unsaponifiable matter in oils and fats, the results of which were embodied in Report No. 1 (ANALYST, 1933, **58**, 203), the Sub-Committee was re-constituted in June, 1933, as follows:

Nominated by the Government Chemist.—F. R. Ennos, B.A., B.Sc., F.I.C.

Nominated by the London Chamber of Commerce and by Messrs. Unilever, Ltd.—L. V. Cocks, F.I.C., and B. D. W. Luff, F.I.C.

Nominated by the London Oil and Tallow Trades Association.—E. R. Bolton, F.I.C.

Nominated by the Society of Public Analysts and Other Analytical Chemists.—P. L. Bean, A.R.C.S., A.I.C., H. E. Cox, D.Sc., F.I.C., D. E. Davis, B.Sc., F.I.C., N. Evers, B.Sc., F.I.C., and W. H. Simmons, B.Sc., F.I.C.

Mr. P. L. Bean had to retire in June, 1934, owing to illness, and Mr. D. E. Davis was appointed in his stead.

Mr. L. V. Cocks was appointed Chairman and Mr. N. Evers Honorary Secretary. Later, owing to a new appointment, Mr. L. V. Cocks was unfortunately compelled to resign, and Dr. H. E. Cox was appointed Chairman. Mr. B. D. W. Luff, F.I.C., was nominated as the representative of the London Chamber of Commerce and of Messrs. Unilever, Ltd., in place of Mr. Cocks.

The Sub-Committee has held eight meetings, and each member has carried out a considerable amount of experimental work.

PUBLISHED METHODS.—A survey of published methods has been made, but none was found to be wholly satisfactory. In most of the earlier books and papers methods are given which involve the extraction of the dried and powdered soap with a solvent. The Sub-Committee finds that such processes are quite unreliable; it is impossible to extract all the fat by any dry process. Methods depending upon wet extraction with ether or petroleum spirit have been put forward recently by some authors (*e.g.* E. L. Smith, ANALYST, 1931, **56**, 9; H. P. Trevithick, *Oil and Fat Ind.*, 1931, **8**, 257; S. Kawai and R. Tonoike, *J. Soc. Chem. Ind. Japan*, 1931, **34**, 153), as well as by the U.S.A. Bureau of Standards in 1916 (*cf.* ANALYST, 1917, **42**, 205), but the conditions there laid down for the extraction of the unsaponified saponifiable matter are not, in our opinion, sufficient for complete extraction. Moreover, the Sub-Committee considers that it is essential to use ether, notwithstanding its greater solvent power for soap, rather than petroleum spirit. For each of the determinations specified, strict adherence to the prescribed details is essential for accurate results.

DEFINITIONS.—Although the terms of reference to the Sub-Committee included the expression "free fat," the Sub-Committee does not regard this term as entirely satisfactory. There appears to be some ambiguity as to whether "free fat" includes free fatty acids or not. Having regard to the fact that soap may be prepared from fatty acids instead of from glycerides, in which case the unsaponified saponifiable matter may consist chiefly of fatty acids, it appears to be necessary to make this point clear. As will be shown later, separate analytical operations are necessary in order to determine the free fatty acids and the unsaponified glycerides, and therefore it is desirable that these two quantities should be expressed separately and be added together if the analyst wishes to do so in order to obtain the total unsaponified saponifiable matter.

The Sub-Committee therefore proposes the following definitions:

(*a*) *Unsaponified neutral fat* for the unsaponified neutral glycerides.

(*b*) *Total unsaponified matter* for the sum of free fatty acids, unsaponified neutral fat and unsaponifiable matter.

(*c*) *Total free fat or total unsaponified saponifiable matter* for the sum of the free fatty acids and the unsaponified neutral fat.

RECOMMENDED METHODS.—The Sub-Committee recommends that the following three determinations should be carried out:

(i) *Free fatty acids* by direct titration;

(ii) *Unsaponified neutral fat*, together with unsaponifiable matter, by the prescribed method of extraction, and

(iii) *Unsaponifiable matter* by saponification and extraction of (ii).

Hence the *unsaponified neutral fat* is (ii)–(iii), and the *total free fat* or *unsaponified saponifiable matter* is (ii) — (iii) + (i).

THE DETERMINATION OF FREE FATTY ACIDS.—Boil 100 ml. of redistilled industrial methylated spirit (66 o.p.)* in a 400-ml. conical flask, add 0·5 ml. of a 0·5 per cent. alcoholic solution of phenolphthalein, allow to cool to 70° C., and neutralise at that temperature with 0·1 *N* alcoholic potassium hydroxide solution. Add 5 g. of the soap in thin shavings and dissolve it as quickly as possible by heating. If the solution is not already alkaline, titrate with 0·1 *N* alcoholic potassium hydroxide solution until a faint pink colour persists for 15 seconds, maintaining the temperature at 70° C. throughout the titration.

Calculate the percentage of free fatty acids in the soap from this titration, expressing it as a percentage of oleic acid (mol. wt. 282). It is allowable for the analyst to express his results in terms of some other acid of different molecular weight, provided that he makes it clear that this has been done. In some circumstances it may be desirable to determine the mean molecular weight of the total fatty acids present after separating them from the soap. The molecular weight should then be stated.

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* *i.e.* 94·7 per cent. by volume of alcohol.

In the analysis of soaps containing an unusually large proportion of matter insoluble in alcohol it may be desirable to filter the solution before titration, but such a procedure may cause a slight increase in the apparent free fatty acid present.

THE DETERMINATION OF UNSAPONIFIED NEUTRAL FAT AND UNSAPONIFIABLE MATTER.—Weigh 5 g. of the soap in thin shavings and dissolve it in about 80 ml. of a mixture of 50 ml. of redistilled industrial methylated spirit (66 o.p.) and 100 ml. of water without heating more than is necessary; transfer to a 500-ml. separating funnel, washing the beaker with the remaining 70 ml. of the dilute alcohol. Extract with 100 ml. of ethyl ether while still slightly warm, run off the alcoholic soap layer into a second separating funnel and repeat the extraction with 50 ml. of ether. Extract the lower layer again with a further 50 ml. of ether, and pour the three ethereal extracts into a separating funnel containing 20 ml. of water. Rotate the separating funnel gently without violent shaking and, after allowing to separate, run off the wash water. Repeat the washing with water in this way until the water run off is not more than faintly turbid on acidification. Wash the ethereal solution twice further by shaking vigorously with 20 ml. of 0·5 *N* aqueous potassium hydroxide solution, each washing with alkali being immediately followed by washing with 20 ml. of water, shaking vigorously each time. Acidify the last washing with alkali after separating it, and, if the liquid becomes turbid, repeat the washings with alkali and water until the final washing with potassium hydroxide remains clear on acidification. Finally, wash with successive quantities of 20 ml. of water until the water no longer gives a pink colour with phenolphthalein. Transfer the ethereal solution to a weighed flask and distil off the ether. When nearly all the ether is evaporated, add 2 to 3 ml. of acetone. By the aid of a gentle current of air remove the solvent completely from the flask, which is preferably almost entirely immersed, held obliquely and rotated in a boiling water-bath. Repeat this operation until the weight is constant. The residue obtained consists of unsaponified neutral fat and unsaponifiable matter.

After weighing, dissolve the contents of the flask in 10 ml. of freshly boiled and neutralised industrial spirit, and titrate with 0·1 *N* alcoholic potassium hydroxide solution to phenolphthalein; not more than 0·1 ml. should be required for neutralisation. If more is required, the test has not been effectively carried out and must be repeated.

THE DETERMINATION OF UNSAPONIFIABLE MATTER.—Evaporate the solution remaining from the above titration until the bulk of the alcohol is removed. Add 25 ml. of 0·5 *N* alcoholic potassium hydroxide and boil under a reflux condenser for half an hour. Transfer the alcoholic soap solution to a separating funnel by the aid of 50 ml. of water, and repeat the process of ether extraction, washing, etc., described above. Weigh the final residue of unsaponifiable matter. Subtraction of this weight from the weight obtained above gives unsaponified neutral fat.

Note.—The methods described above are applicable to most ordinary soaps, but cannot always be applied without some modification to special types, such as filled, medicated or highly perfumed soaps.

EXPERIMENTAL

THE DETERMINATION OF FREE FATTY ACIDS.—Much attention has been given to the precise conditions for the titration of free acidity. It has been found necessary to adhere closely to the conditions laid down in the above description of the method for accurate results. The following points resulting from the work on this subject are worthy of mention:

(*a*) *The Indicator.*—It has been found by electrometric methods that, in the titration of fatty acids with alcoholic potash at 70° C., the point of neutralisation corresponds sufficiently closely for practical purposes to the change of colour of phenolphthalein when 0·5 ml. of a 0·5 per cent. alcoholic solution of the indicator is present in 100 ml. of the alcoholic soap solution. A larger quantity is liable to give low results, and less to give high results. This indicator is therefore the most suitable for the titration.

(*b*) *Filtration.*—Experiments have been made to find the reason for the often-observed fact that a faintly alkaline alcoholic solution, with or without soap, becomes less alkaline or even slightly acid to phenolphthalein after filtration. It was shown that the chief cause of this production of acidity was the absorption of carbon dioxide during filtration, although there are other factors involved. In the case of the determination of free fatty acids in a soap which is only faintly acid, filtration may give rise to an error of the order of 0·3 ml. 0·1 *N* on 5 g. of soap, or a soap which is faintly alkaline may be made to appear slightly acid by filtration, but these errors are negligible when appreciable amounts of free fatty acids are present.

(*c*) *Quantity of Soap to be taken.*—While it was recognised that more accurate results could be obtained by using a large quantity of soap, 5 g. was regarded as the largest quantity that could be recommended for a general method.

(*d*) *Alternative Methods.*—A study has been made of two variations in the titration method which may be found useful in certain circumstances.

> *The Barium Chloride Method.*—There is a possibility of the co-existence in soap of free fatty acid and sodium carbonate. It has been found that when such a soap is dissolved in alcohol some interaction takes place, although if dry sodium carbonate be added to an alcoholic solution of soap containing free fatty acid, no reaction takes place.
>
> When it is desired to titrate free fatty acid in the presence of sodium carbonate, this may be effected by adding 1 ml. of a neutral 10 per cent. aqueous solution of barium chloride to the neutralised alcohol, dissolving the soap in the boiling mixture, and titrating the free fatty acid without filtration; the effect of the sodium carbonate is thus eliminated.
>
> *The Glycerin Method.*—In order that the titration might be carried out at laboratory temperature without jellying of the soap solution, it was found convenient to use a mixture of alcohol and glycerin (80 : 20 by volume) as the solvent. In preparing this, a slight excess of alkali should be added to the glycerin-alcohol mixture, and the whole saponified, then made slightly acid and adjusted to neutrality to phenolphthalein at 15° C. by the cautious addition of 0·1 *N* alcoholic potassium hydroxide solution. Five g. of soap are soluble when warmed with 100 ml. of this solvent, and accurate results are obtained at 15° C.

THE EXTRACTION OF UNSAPONIFIED NEUTRAL FAT AND UNSAPONIFIABLE MATTER.—Methods for the dry extraction of the soap by solvents were abandoned as unsatisfactory. Experiments on the extraction of the soap solution with petroleum spirit in order to obtain the total unsaponified matter, followed by another extraction under the same conditions after neutralisation, to obtain the unsaponified neutral fat + unsaponifiable matter, and so to calculate the free fatty acids by difference, also gave unsatisfactory results. Experiments on the application of the method recommended in Report No. 1 to the determination of unsaponified neutral fat + unsaponifiable matter showed that certain modifications in the washing procedure were desirable. These modifications appear in the recommended method. The addition of potassium hydroxide to the soap solution before extraction with ether did not affect the results.

RESULTS

The following table gives the results obtained by the recommended methods on two soaps and shows the variations that may be expected between different analysts using these methods.

Soap C

Observer	Free fatty acids as oleic acid Per Cent.	Unsaponifiable matter Per Cent.	Unsaponified neutral fat Per Cent.
A	0·15	0·81	0·10
B	0·20	0·81	0·02
C	0·17	0·82	0·06
D	0·13	—	—
E	0·14	0·87	0·06
F	0·15	0·82	0·04
		Soap D	
A	0·60	0·49	0·42
B	0·74	0·46	0·30
C	0·74	0·44	0·40
D	0·56	—	—
E	0·63	0·42	0·36
F	0·67	0·43	0·45

B.P. STANDARDS.—The standards of the British Pharmacopoeia for free fat in soaps were considered to be unsatisfactory. A note was inserted in THE ANALYST (1934, 59, 104) drawing attention to this, and suggesting the revision of these limits.

(*Signed*) H. E. COX (*Chairman*)
NORMAN EVERS (*Hon. Secretary*)

21*st May*, 1935

Second Report of the Sub-Committee on the Determination of Arsenic, Lead, and other Poisonous Metals in Food-colouring Materials to the Analytical Methods Committee of the Society of Public Analysts

II. THE DETERMINATION OF LEAD

THE Sub-Committee was convened by the Standing Committee, and consists of the following members:

T. Callan, M.Sc., Ph.D., F.I.C. (Chairman), nominated by Imperial Chemical Industries, Ltd. (Dyestuffs Group).

S. G. Clifford, A.I.C. (Hon. Sec.), nominated by the Oil and Colour Chemists' Association.

H. Drake-Law, D.Sc., F.I.C., and W. G. Messenger, B.Sc., F.I.C., nominated by the Society of Public Analysts and other Analytical Chemists.

T. Macara, F.I.C., nominated by the British Association of Research for the Cocoa, Chocolate, Sugar, Confectionery and Jam Trades.

J. R. Nicholls, B.Sc., F.I.C., nominated by the Government Chemist.

N. Strafford, M.Sc., F.I.C., nominated by Imperial Chemical Industries, Ltd. (Dyestuffs Group).

The present report deals with the determination of lead in food-colouring materials. Any general method for this purpose must be applicable to colours containing variable amounts of a large range of inorganic substances which may be present in the commercial article. It was early realised by the Sub-Committee that such a method must, of necessity, be more complicated than one designed for particular colours where the impurities are limited.

The procedure for the destructive wet-oxidation of the colouring materials having previously been standardised (see First Report, ANALYST, 1930, **55**, 102 *et seq.*), the possibility of determining the lead in the solution remaining after the removal of arsenic by distillation was investigated, since this would obviously result in considerable economy of time and material. Whilst the work described in the present report is primarily concerned with the determination of lead, the feasibility of providing for the simultaneous determination of other metals was constantly kept in mind, and the method finally recommended has the advantage that, in addition to lead, copper is quantitatively separated, and may be determined by a suitable procedure.

The method for the determination of copper will be dealt with in the third report of the Committee to be issued at a later date.

In the first place the Committee critically reviewed methods available for the determination of small amounts of lead when present in a solution free from interfering substances, both inorganic and organic. After consideration of the various methods available, the conclusion was reached that the colorimetric determination by means of the lead sulphide produced in alkaline solution was the method most suitable for general use.

The subsequent experimental investigation, therefore, resolved itself into a study of the conditions best adapted to the application of the colorimetric sulphide method to the determination of lead in commonly occurring food-colouring materials.

It is well known that the presence of a number of substances, *e.g.* aluminium and iron salts, calcium and magnesium phosphates, etc., interferes seriously with the determination of lead by the colorimetric sulphide method, and, broadly speaking, the investigation was mainly concerned with overcoming or eliminating the disturbing effects caused by such substances.

DIRECT METHOD.—Attention was first concentrated on what may be termed the "Direct Method," in which, prior to applying the colorimetric test, no attempt is made to separate the lead from other metals which might be present. Such a method requires complete destruction of the organic matter by the wet combustion, for even traces of residual nitro-bodies may give yellowish solutions, the colour becoming intensified in ammoniacal solution.

This method was very thoroughly investigated, since it possesses the obvious advantages of simplicity and rapidity.

In the case of most samples of food-colouring materials, the only heavy metals likely to be present which would interfere with the determination of lead as sulphide are iron and copper. The interference of these metals can, however, be avoided by conversion into complex cyanides by treatment with an ammoniacal cyanide solution under suitable conditions. It was found that to effect quantitative conversion, and also to obtain a colourless solution prior to the lead sulphide precipitation, very special precautions were required. In particular, complete reduction of the ferric salts was found to be essential, and for this purpose a number of reducing agents, *e.g.* sodium metabisulphite and sodium thiosulphate, were examined. Conditions were eventually established where by using a rigidly defined procedure the interference of iron could be prevented, provided the original colouring material did not contain more than about 200 parts of iron per million. Beyond this amount of iron the colour of the ferrocyanide produced interfered with the subsequent colorimetric determination of the lead.

It was recognised, however, that an appreciable amount of iron in food-colouring materials is not considered deleterious, and consequently the necessity for providing for the possible presence of iron in relatively large amounts was realised to be of importance.

A study was also made of the effect of other metals—antimony, tin and zinc—and of phosphates, particularly in the presence of aluminium, calcium and magnesium salts. It was established that amounts of antimony, tin and zinc up to, and possibly exceeding, 100 parts per million have no noticeable effect on the accuracy of the direct lead determination.

It was found, however, that the presence of calcium and magnesium phosphates leads to difficulties in the colorimetric comparisons owing to production of a turbidity, whilst aluminium salts even in quite small amounts greatly reduce the intensity of the colour of the colloidal lead sulphide, leading to low and erratic results. This, no doubt, is due to occlusion of some of the lead salt by the aluminium hydroxide precipitate. In the absence of phosphates it was found that the disturbing effects of aluminium, calcium and magnesium salts can be avoided by the addition of an alkali citrate or tartrate, but in the presence of phosphates of magnesium and aluminium no method of avoiding their interference could be found.

In many cases where the amount of lead present in the sample was very small, of the order for example of 5 parts per million, the results were not entirely satisfactory, because the final tint of the lead sulphide in the test solution was necessarily very weak and not quite identical with that in the standard comparison solutions.

Thus the direct method fails in three cases, namely, when much iron is present, when phosphates of magnesium and aluminium are present, and when the lead-content is very low.

For the special cases of samples containing relatively large amounts of iron, a method for the removal of the major proportion of the iron (as ferric chloride) by extraction with ether after addition of hydrochloric acid, was investigated.

Whilst this method gave reasonably satisfactory results when large amounts of iron were present, it possesses several disadvantages. The sulphuric acid remaining from the wet-oxidation process interferes with the extraction of the ferric chloride by ether and must therefore be removed. Further, the relatively large amount of hydrochloric acid must be removed after extraction of the iron, before the determination of the lead can be completed.

It became increasingly evident that in a generally applicable method, separation of the lead from interfering substances was essential, and several methods which appeared likely to be suitable were next examined.

Separation of Lead by Electrolysis.—An accurate method for the determination of small quantities of lead in biological materials has been described by Francis, Harvey and Buchan (Analyst, 1929, **54**, 725).

The process, after destruction of organic matter, involves, amongst other steps, the electrolytic deposition of lead as peroxide. This separation of lead has great advantages where such metals as bismuth are present, but having regard to the impurities likely to be present in food-colouring materials and to the fact that iron in appreciable amounts causes interference, it was considered advisable to avoid this refinement if possible. Subsequent work showed that lead could satisfactorily be separated and determined without resort to electrolysis.

Separation of Lead by Diphenylthiocarbazone.—A new method for the separation of lead has been described by Allport and Skrimshire (Analyst, 1932, **57**, 440). The method depends upon the extraction of the lead from ammoniacal solution by means of a chloroform solution of diphenylthiocarbazone. The precipitation of certain metallic hydroxides, *e.g.* iron, in the ammoniacal solution is prevented by the addition of citrate solution, and cyanide solution is added to prevent extraction of some other metals. The lead is finally determined colorimetrically as sulphide. This method has been tested on a number of dyes by some members of the Sub-Committee, and in many cases excellent results have been obtained. With certain samples, however, the lead has been only partially or not at all extracted, and it appears that in these cases the ammoniacal solution has contained insoluble matter which has occluded some of the lead and inhibited its extraction by the organic solvent. It has been found that in certain cases traces of insoluble matter may be sufficient to prevent the recovery of quite appreciable proportions of the lead where the amount present is of the order of 20 parts per million. In the case of dyestuffs it is not possible to ensure that the solutions to be extracted, containing as they may phosphates, silicates, salts of iron, aluminium, calcium, magnesium, etc., shall be in all cases free from insoluble matter which may retain a portion of the lead. Accordingly there can be no general certainty that the whole of the lead is recovered.

A further disadvantage of this extraction method is that it does not differentiate between lead and bismuth. The presence of small quantities of the latter might not be suspected, and would be determined as lead. Whilst bismuth is not regarded as a likely impurity in dyes, the possibility of its presence cannot be ignored.

In the opinion of the Sub-Committee this extraction method, although perfectly satisfactory in the majority of cases, is not, at present, of general application.

THE DIRECT SULPHATE PRECIPITATION METHOD.—This method depends upon the separation of the lead as lead sulphate from a water-acid-alcohol solution, and was applied directly to the residue obtained after wet-oxidation and removal of the arsenic by distillation. Since the residue usually contains an appreciable amount of inorganic salts (chiefly sodium and ammonium sulphates), it was necessary to precipitate the lead as sulphate from a relatively large volume of solution. In general, about 150 ml. of 30 to 33 per cent. alcohol were used (where 5 g. of dyestuff had been oxidised).

Preliminary work on this method was carried out on suitable solutions containing known amounts of iron, lead and copper. It was early recognised that lead sulphate was very slightly, but measurably, soluble in the alcohol-water-sulphuric acid mixture (containing also inorganic salts). In the absence of considerable amounts of iron salts, it was found that although the amounts of lead lost in the filtrate could not be expressed by a definite figure (in the hands of different workers it varied from 0·00002 g. to 0·00007 g. of Pb in the volume of liquid used, *i.e.* 150 ml.), yet in the hands of the same worker it remained reasonably constant.

Using so-called "lead free" reagents, this solubility was sometimes greater than the minute amount of lead present in the reagents, and in consequence the blank determination showed no lead, so that it was impossible to know whether the solution was saturated with respect to lead sulphate and, hence, impossible to apply any correction.

The solubility of the lead sulphate was accordingly approximately compensated for by the addition of a definite quantity of standard lead solution both to the test and blank solutions, to ensure that in both solutions lead sulphate was precipitated. By difference the amount of lead present in the sample was obtained.

In efforts to perfect this promising method, which was very fully investigated, everything possible was done to define and standardise rigidly all the conditions governing the procedure, *e.g.* concentration of acid and alcohol, methods of addition of water-alcohol mixture, and of isolation of the lead sulphate by filtration. It is worthy of mention that in the case of a dyestuff containing lead to the extent of 20 parts per million or less, the precipitated lead sulphate is quite invisible to the naked eye. It was proved, however, that by filtration through pulped filter paper in a Gooch crucible the lead sulphate precipitate was satisfactorily retained.

It was found possible to define conditions which would give fairly accurate results when applied to standard lead solutions containing relatively small proportions of iron and copper.

When, however, this direct sulphate precipitation method was applied to solutions of known composition containing large amounts of iron (equivalent to test on a dyestuff containing—say—50,000 parts of iron per million) difficulty was experienced in manipulation, owing to the sparing solubility of the ferric sulphate in the dilute acid-alcohol mixture. This was overcome by warming the solution to dissolve the ferric sulphate, and then leaving the solution to stand overnight to precipitate the lead sulphate. The results obtained for lead were, however, erratic and low as a rule, possibly owing to the increased solubility of the lead sulphate in the presence of ferric sulphate. For example, in the case of a test solution of ferric chloride containing the equivalent of 22 parts per million of lead the nett amounts of lead recovered by individual members of the committee varied from nil to 29 parts per million.

It was therefore clear that, although the method was of value in many cases, it failed in the presence of large amounts of iron. The Sub-Committee has throughout the investigation aimed at providing a method of general application, and accordingly cannot recommend the direct sulphate precipitation method.

SULPHIDE-SULPHATE PRECIPITATION METHOD.—Since the quantitative separation of lead as sulphate was found impossible in the presence of large amounts of salts, particularly of ferric salts, methods based on the preliminary separation of lead as sulphide were next investigated.

Francis, Harvey and Buchan (*loc. cit.*) add a small quantity of copper to ensure co-precipitation of lead. For the present purpose such addition is undesirable, since it would prevent the subsequent determination of copper, if required.

Conditions have been established whereby it is possible to precipitate quantitatively the sulphides of lead and copper with only a very small proportion of ferrous sulphide, this result being achieved by careful control of the *p*H value of the solution from which the sulphides are precipitated. Salts of other metals, *e.g.* calcium, aluminium and alkali metals, some of which will always be present in relatively large proportions, remain in the filtrate and are rejected.

The precipitated sulphides and the filter paper on which they are retained may be brought into solution by wet oxidation, and the lead is determined colorimetrically, with satisfactory results in many cases, after eliminating the effect of the copper and any remaining traces of iron by conversion to complex cyanides. In view of the fact, however, that the solution of the precipitated sulphides is obtained virtually free from substances interfering with the quantitative precipitation of lead as sulphate (see "Direct Sulphate Method"), it was deemed advisable to take advantage of this and to isolate the lead from the sulphide precipitate containing the copper and traces of iron, by conversion to sulphate. In addition, this procedure has the advantage that copper is separated from the lead and may subsequently be determined.

Under the conditions described later the lead sulphate is precipitated from a small volume of alcohol-water-sulphuric acid practically free from salts, and the Sub-Committee is satisfied that recovery of the lead is quantitative, the solubility of lead sulphate in the volume used being negligible. The completeness of the recovery of the lead may be judged from the fact that the lead-content of the "lead-free" reagents employed may be determined by the identical method employed for the analysis of the dyestuff. The results obtained agree closely with those obtained by a direct colorimetric determination of the lead in the reagents.

The remaining traces of iron, and any other interfering metals likely to be present, are very effectively removed by this process. It may be mentioned that the method has been applied to iron oxide with complete success, and that quantities of bismuth up to 200 parts per million do not interfere. After thorough trial the Sub-Committee recommends it as being the best method available for general use.

Special attention has been paid to the case of two food-colouring materials containing appreciable quantities of silica and alumina, namely, Ultramarine and Carmine Nacarat.

When such substances are treated in the usual manner, the solution after wet oxidation contains varying amounts of insoluble residue which may consist of aluminium sulphate, or silica, or both. The aluminium sulphate, which may retain lead, will not readily dissolve even after dilution with water and heating, and it may be necessary to digest for some time to ensure complete solution. Silica will, of course, remain insoluble, and it has been shown to retain a large proportion of the lead. It is not, therefore, permissible to filter off the precipitate and to reject it. It has been found, however, that by extracting the insoluble residue with boiling dilute hydrochloric acid, the whole of the retained lead may be recovered.

As an example, the figures representing the lead contained in the first acid filtrate and the subsequent hydrochloric acid extract, and in the final residue obtained in the analysis of samples of Ultramarine and Carmine Nacarat are given below. The figures quoted are in terms of parts per million of dye.

	Ultramarine			Carmine		
	(1)	(2)	(3)	(1)	(2)	(3)
First acid filtrate and washings	22	12	15	8	4	6
Hydrochloric acid extract of residual precipitate	2	10	6	20	20	20
Final residue*	less than 1 in each case			less than 1 in each case		

Whilst it has been shown that extraction with hydrochloric acid completely removes lead from the precipitated silica, in the case of Ultramarine the precipitate of hydrated silica produced after the initial nitric-sulphuric acid digestion is so voluminous that its manipulation is difficult. Accordingly the general method described in the present report is not recommended for Ultramarine, and the Committee recommends that in the case of Ultramarine the lead be determined on a separate portion of the sample and not on the residue from the arsenic determination. A special note is appended to the general method for its particular treatment.

When large amounts of aluminium are present the greater portion is eliminated by the sulphide precipitation process. The filter paper containing the mixed sulphides may, however, retain small amounts of aluminium salts, and care should be taken to remove these by washing with hydrogen sulphide water.

If the aluminium salts are incompletely washed away, a little aluminium sulphate may separate from the solution obtained after the wet-oxidation of the filter paper and sulphides. The aluminium sulphate of course remains with the lead sulphate and some aluminium may therefore be present in the ammonium acetate extract on which the colorimetric determination of the lead is carried out.

It has already been mentioned that even traces of aluminium interfere with the colorimetric determination of lead as sulphide, low results being obtained. By the addition of citrate, however, this interference is entirely prevented.

The method as finally adopted by the Sub-Committee is given in the Appendix.

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* The final residue was "fumed" with sulphuric acid and hydrofluoric acid to remove silica and then extracted with boiling hydrochloric acid.

The following table shows the food-colouring materials circulated and the results obtained by the various members of the Sub-Committee employing the method as described:

	Lead-content expressed as parts Pb per million.				
	A	B	C	D	E
Tartrazine	15	16	20	16	13
Ponceau 2R	22	25	20	22	19
Rhodamine B. conc.*	234	212	243	271	231
Carmine Nacarat (15)	—	18	14	13	17
„ „ (16)	—	31	40	29	35
Bismarck brown	24	27	28	24	24
Naphthol Yellow S.	17	21	20	19	19
Blue F.C.F.	28	29	30	32	30
Methylene Blue	20	28	24	23	28
Nigrosine	38	38	38	38	40
Ferric Oxide	360	405	405	380	385
Caramel	7	9	11	6	7
Yellow O.B.	8	9	8	6	6
Ultramarine 23	91	94	103	115	100
Lead solution (10 ml.=5 g. of dye)†	21	27	25	25	22
10 ml. lead solution plus 5 g. of ammonium alum	38	40	39	39	40
Ammonium alum	15	15	11	14	15

* This sample was not of food-colouring quality. It was circulated with a view to determining the reproducibility of the results obtained on a sample of abnormally high lead-content.

† Ten ml. of this solution were subjected to the complete process. They were taken as the equivalent of 5 g. of dye. The lead found is reported as parts per million on the hypothetical dye. The solution actually contained the equivalent of 25 parts of lead per million on this basis.

In assessing the accuracy of the method it should be noted that the final result includes errors incidental to (i) the process of separating the lead, (ii) the colorimetric determination of the lead.

The Sub-Committee decided to examine the accuracy of the colorimetric determination in order to obtain some indication as to the relative effect of these two sources of experimental error. A number of observers in the laboratories of four members of the Committee carried out independent comparisons of given lead solutions of known compositions against the appropriate series of standards, prepared exactly as described in the method. The actual composition of the standard was unknown to the observers. The errors of comparison, expressed as a percentage of the known lead-content, are summarised in the table on page 548.

From this it will be observed that in each of the four laboratories the extreme error was of the order of plus or minus 8 per cent., irrespective of the amount of lead under determination.

In considering the contribution of this error to the total error of the method it should be borne in mind that each final result is the difference between two colorimetric determinations, *viz.* that of the test solution and that of the blank.

The magnitude of the summation of these two possible errors depends on the lead-content of (*a*) the sample, and (*b*) the blank.

Whilst it is fully realised that there will be few cases in which the total error of the colorimetric determination will be the sum of the two extreme errors, it should be observed how the extreme error varies with the amount of lead present.

COLORIMETRIC DETERMINATION OF LEAD AS SULPHIDE

Summary of results obtained by visual comparison.—The figures represent the percentage of error in the determination of known amounts of lead.

Laboratory	Observer	Range of test ml. Pb solution (1 ml. = 0·00001 gm. Pb)					
		3·6–4·4	5·6–6·4	7·4–8·6	9·4–10·6	11·1–12·9	12·8–15·0
A	1	nil	+3	nil	−1½	nil	+3
	2	nil	+6½	−2	+1½	−2½	−3
	3	−2½	+6½	+4	−6½	—	—
	4	nil	+3	+5½	−6½	nil	−3
	5	−5	—	+4	—	—	—
	6	−7½	—	+4	+7½	+7½	—
	7	—	—	—	—	+5	+3
	8	—	—	—	—	—	+3
B	1	−5	+6½	—	+6	—	−6
	2	−5	—	nil	—	−5	—
	3	+5	−3	−2½	+4	−2½	−3
	4	−5	nil	—	−2	−2½	−3
		—	—	nil	+2	—	—
		—	nil	−2½	—	—	—
		—	—	—	—	−5	−6
C		−3	−3	+2½	−4	+2½	nil
		−5	−6½	−7½	−6	+7	+6
		−5	+3	nil	−4	+2½	nil
		−5	+6½	−5	−4	+2½	nil
D	1	5	+3	nil	nil	nil	−3
	2	5	+7	nil	nil	−3½	−6
	3	5	+3	−7½	+2	+5	−3
Extreme error, per cent.		−7½	+7	−7½	+7½	+7½	−8
Mean error, per cent.		4	4	3	3½	3½	3½

In the following table it is assumed that the "blank" is 5 ml. of standard dilute lead solution (equivalent to 10 parts of lead per million calculated on 5 g. of the colouring material), a not unusual figure.

Lead as parts per million						Extreme error expressed as per cent. of the lead in sample ±
In sample	In blank	Possible error on blank ± (A)	In test	Possible error in test ± (B)	Total possible error ± (A) + (B)	
10	10	0·8	20	1·6	2·4	24
20	10	0·8	30	2·4	3·2	16
50	10	0·8	60	4·8	5·6	11
100	10	0·8	110	8·8	9·6	9½
400	10	0·8	410	32·8	33·6	8

Whilst the actual error in the great majority of cases will be less than that shown in the last column, the results indicate how the accuracy of the method increases as the amount of lead under determination increases.

An analysis of the results obtained on the circulated samples by the various members of the Sub-Committee shows that the extreme variations from the mean results may be expressed as follows:

Sample	Extreme p.p.m.	Mean p.p.m.	Maximum deviation ±	Maximum deviation, expressed as per cent. of mean ±
Yellow O.B.	6–9	7½	1½	20
Caramel	6–11	8½	2½	30
Alum	11–15	13	2	15
Carmine Nacarat (15)	13–18	15½	2½	16
Tartrazine	13–20	16½	3½	21
Naphthol Yellow S.	17–21	19	2	11
Ponceau 2R	19–25	22	3	14
Methylene Blue	20–28	24	4	17
Lead solution	21–27	24	3	13
Bismarck Brown	24–28	26	2	8
Blue F.C.F.	28–32	30	2	7
Carmine Nacarat (16)	29–40	34½	5½	16
Nigrosine	38–40	39	1	3
Lead solution plus alum	38–40	39	1	3
Ultramarine	91–115	103	12	12
Rhodamine B	212–271	241½	29½	12
Ferric Oxide	360–405	382½	22½	6

A comparison of this table with the preceding one shows that the actual colorimetric determination of the lead is responsible for a large proportion of the overall error of the method. A study by two members of the Sub-Committee of the colloidal lead sulphide "solutions" revealed that the transmission of light by two similarly prepared solutions, apparently equal in shade to the eye, may be appreciably different when measured by the photo-electric cell.

The Sub-Committee is of opinion that it will not be possible to attain a higher degree of accuracy than that found in the present investigation until the colloidal sulphide method has been replaced by a true colorimetric method in which the absorption of light due to a given amount of lead is accurately reproducible. This will best be attained if the coloured lead complex is in true solution.

The Sub-Committee is therefore directing its attention to devising such a method.

For, and on behalf of, the Sub-Committee,

(*Signed*) T. CALLAN (*Chairman*)
S. G. CLIFFORD (*Hon. Sec.*)

20*th* *June*, 1935

APPENDIX

List of Reagents

1. *Concentrated Nitric Acid.*—Sp.gr. 1·42. Strength approx. 70 per cent. wt/wt.
2. *Dilute Nitric Acid.*—Concentrated nitric acid is mixed with an equal volume of distilled water.
3. *Dilute Hydrochloric Acid.*—Concentrated hydrochloric acid sp.gr. 1·16. Strength approx. 32 per cent. wt/wt is mixed with an equal volume of distilled water.
4. *Concentrated Ammonia.*—Sp.gr. 0·880.

5. *Dilute Ammonia.*—One volume of concentrated ammonia is mixed with two volumes of water.
6. *Very Dilute Ammonia.*—One volume of concentrated ammonia is mixed with ten volumes of water.
7. *Concentrated Sulphuric Acid.*—Sp.gr. 1·84. Strength approx. 95 per cent. wt/wt.
8. *Alcohol-water Mixture.*—One volume of industrial methylated spirits, 64°O.P., is mixed with 2 volumes of distilled water.
9. *Alcohol-Water-Sulphuric Acid Mixture.*—10 volumes of industrial methylated spirits, and 20 volumes of water, and 1 volume of concentrated sulphuric acid are mixed together.
10. *Ammonium Acetate Solution.*—100 g. of ammonium acetate are dissolved in 100 ml. of distilled water.
11. *Dilute Ammonium Acetate Solution.*—10 g. of ammonium acetate are dissolved in distilled water and diluted to 100 ml.
12. *Potassium Cyanide Solution.*—10 g. of potassium cyanide are dissolved in distilled water and diluted to 100 ml.
13. *Ammonium Citrate Solution.*—10 g. of ammonium citrate are dissolved in distilled water and diluted to 100 ml.
14. *Sodium Sulphide Solution.*—10 g. of pure white sodium sulphide crystals are dissolved in distilled water and diluted to 100 ml.
15. *Hydrofluoric Acid.*—40 to 50 per cent.
16. *Standard Lead Solution.*—A solution containing 0·01 mg. of lead in 1 ml. 0·1 g. of pure lead foil or 0·16 g. of pure lead nitrate is dissolved in dilute nitric acid and diluted to 100 ml. with dilute nitric acid. This solution contains 1 mg. of lead in 1 ml. and may be retained as a stock solution. When required for use, 5 ml. of this solution are diluted with water to 500 ml.
17. *Congo Red Papers.*—Sheet filter-paper is dipped in a 0·1 per cent. aqueous solution of purified Congo Red and dried as rapidly as possible in a warm atmosphere free from chemical fumes.
18. *Filter Papers.*—Before use, the filter papers are washed with dilute hydrochloric acid and then with distilled water.

METHOD

Five g. of the sample are treated by the wet oxidation method, and the arsenic removed as described in THE ANALYST, 1930, 55, 102, etc. The residue is treated with 2 ml. of concentrated nitric acid and heated until the sulphuric acid is fuming. The mixture is cooled, diluted with about 100 ml. of distilled water, and warmed until solution is apparently complete.

If any insoluble matter is observed, the solution is filtered and the residue washed with hot water. The paper and residue are boiled with 20 ml. of dilute hydrochloric acid, the solution filtered, the insoluble matter again boiled with distilled water, filtered and washed with hot distilled water. The filtrate and washings are added to the original acid filtrate, and the residue is discarded.

The combined filtrate and washings are transferred to a beaker and diluted to 150 to 200 ml. with water. Concentrated ammonia is added gradually, with stirring, until the major part of the acid has been neutralised. The solution is cooled, and dilute ammonia is added, drop by drop, with stirring, until the solution just fails to change the colour of wet Congo red paper. (If iron is present in appreciable amounts, it acts as an indicator, the end-point being such that the solution is deep yellow in colour and the whole of the iron is just held in solution.)

At this stage there must be no permanent precipitate. Hydrogen sulphide is passed through the solution for at least 15 minutes to reduce any iron present to the ferrous condition. The solution is quickly heated to about 50° C., and, while still warm, very dilute ammonia is added until the solution just fails to react acid to Congo red paper. The addition of ammonia at this stage must be made slowly and carefully, with constant stirring to avoid precipitation of iron, aluminium, calcium, etc. If the end-point is passed, the solution should be made just acid by the addition of a few drops of dilute hydrochloric acid and again brought to the neutral point to Congo red. After standing for 15 minutes with occasional stirring, the solution is filtered through a folded filter paper (similar to Whatman No. 1). The precipitate is washed twice with 10 ml. of saturated aqueous solution of hydrogen sulphide.

The filter paper and precipitate are transferred to the original digestion flask, the beaker washed with hot dilute nitric acid, using 20 ml. in all, and the washings added to the flask. One ml. of concentrated sulphuric acid is added, and the contents of the flask are digested over a Bunsen flame, using an asbestos square support having a circular aperture of 3 cm. diameter, until the paper and precipitate are completely oxidised. If oxidation is difficult, a further small quantity of nitric acid is added and the heating continued. This operation is repeated until the solution remains colourless and the sulphuric acid is slightly fuming. The contents of the flask are cooled, 5 ml. of water added, and the solution again heated to fuming. A small amount of aluminium sulphate may be deposited at this stage if fuming is unduly prolonged. Should this deposition occur, its solution is effected by the addition of 5 ml. of water and further careful heating to fuming.

After cooling, 15 ml. of alcohol-water mixture are added, and the contents of the flask are thoroughly mixed and allowed to stand overnight.

The liquid is then filtered slowly (about 1 drop per second) with suction through a Gooch crucible packed with filter paper pulp,* and the flask and crucible are washed with two successive portions of 5 ml. of a mixture of alcohol-water-sulphuric acid in the proportions, 10, 20, 1 by volume. The filtrate is retained for the determination of copper.

Ten ml. of ammonium acetate solution are added to the digestion flask and boiled, care being taken that the liquid comes into contact with the whole of the interior surface of the flask. The solution is poured on to the Gooch crucible and very gentle suction applied, so that the liquid slowly passes through. The flask and crucible are then washed with 10 ml. of hot dilute ammonium acetate solution followed by hot distilled water until the filtrate measures almost 50 ml. The filtrate is cooled, transferred to a 50-ml. or 75-ml. measuring flask, and made up to the mark. The whole of the solution or an aliquot part is transferred to a 100-ml. Nessler cylinder, 5 ml. of ammonium citrate solution, 2 ml. of ammonia, and 4 ml. of potassium cyanide solution are added, and the solution is made up to the mark.

A series of standard comparison solutions are prepared, each containing in the same volume (100 ml.) the quantities of ammonium acetate, ammonium citrate, ammonia and potassium cyanide solutions used in the test, together with varying quantities of standard lead solution. The test solution and standards should be water white. A coloured solution indicates incomplete oxidation, and the solution must be rejected and the whole determination recommenced. Each solution is mixed with 2 ml. of sodium sulphide solution, and the test solution matched against the standard comparison solutions. The volume of the aliquot portion of the test solution taken for colorimetric determination of the lead should be such that the colour produced with sodium sulphide is matched by a standard comparison solution containing preferably about 8 to 12 ml., and, in any case, not more than 15 ml. of standard lead solution.

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* *Preparation of Gooch Crucible.*—About 0·2 g. of Whatman No. 1 or similar filter paper is covered with concentrated hydrochloric acid and rubbed with a glass rod until thoroughly disintegrated. After diluting with water, the mixture is poured into a Gooch crucible having a base of about 2 cm. in diameter, the pulp gently but firmly packed by pressing with a flattened end of a glass rod, and washed until free from acid, using suction.

In order to determine the lead in the reagents (which should be "lead-free") a blank experiment is carried out on the same quantities of reagents as used in the test, the procedure throughout being exactly as described above for the determination of total lead in food-colouring materials.

NOTE.—In the case of Ultramarine the preliminary treatment is carried out in one of the following ways:

(1) Five g. of the sample are weighed into a platinum dish, and mixed with 30 ml. of a cold mixture of equal volumes of sulphuric acid and water, and 2 to 3 ml. of hydrofluoric acid. The mixture is evaporated on the steam bath for 1 hour, treated with more hydrofluoric acid, the mass being stirred with a platinum rod, and again evaporated. This treatment and evaporation may be repeated. The dish is heated on a hot plate until the sulphuric acid is fuming, and, after cooling, the mixture is washed into a "Pyrex"* Kjeldahl flask, the dish being washed out with 10 ml. of boiling dilute hydrochloric acid. The liquid is evaporated, and nitric acid is added in small portions until oxidation is complete. The liquid is again heated to fuming, cooled, diluted with about 100 ml. of distilled water, and warmed until solution is apparently complete.

(2) Five g. of the sample are placed in a silica flask and mixed with 10 ml. of a cold mixture of equal volumes of sulphuric acid and water, and 2 to 3 ml. of hydrofluoric acid. The mixture is heated gently until the initial vigorous action has abated, 10 ml. of sulphuric acid are added, and the mixture again heated. Hydrofluoric acid is added in small portions at intervals until the silica has nearly all been removed. When the liquid is fuming steadily, nitric acid is added in small portions until oxidation is complete. The liquid is again heated to fuming, cooled, diluted with about 100 ml. of distilled water and warmed until solution is apparently complete.

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

METROPOLITAN BOROUGH OF STEPNEY

ANNUAL REPORT OF THE BOROUGH ANALYST FOR THE YEAR 1934

OF the 1614 samples examined under the Food and Drugs (Adulteration) Act, 568 were informal.

HYDROGEN PEROXIDE IN BOTTLED HERRINGS.—Three samples of pickling liquid and 2 samples of "rollmops" (bottled herring) were examined for hydrogen peroxide; hydrogen peroxide was present in 1 sample of pickling liquid. The examination of these samples followed a complaint from a packer that he could not sell his "rollmops," as his competitors had a whiter product which, he said, was artificially produced. The sliced herrings are dipped in a pickling liquid containing hydrogen peroxide and, when sufficiently bleached, are drained and bottled in a liquid free from hydrogen peroxide. The bleaching agent could not, therefore, be detected in the finished product. (In a recent report from Western Australia it was stated that tripe had been examined which had been bleached and "plumped" with sodium peroxide solution forming a whiter product and increasing the weight so that 20 lbs. of tripe produced at least 25 lbs. after treatment. *cf.* ANALYST, 1934, 59, 824.)

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* In view of the known presence of lead in "Pyrex" glass, the possibility of this as a source of error has been exhaustively investigated by one member of the Sub-Committee, and the Sub-Committee is satisfied that there is no danger in the use of such glass.

PEPPER BLEACHED WITH SULPHUR DIOXIDE.—Owing to information from other parts of the country that pepper which had been found to contain sulphur dioxide emanated from a Stepney factory, samples were taken from this firm, but no sulphur dioxide was found. It was admitted, however, that sulphur dioxide was used, but that it was removed before the pepper was sent out; one consignment had, however, been despatched before the treatment had been carried out.

SURGICAL SPIRIT.—There has been much drinking of this spirit. A sample consisted of methylated spirit (92 per cent. alcohol by vol.) containing 5 per cent. of castor oil, so that half a pint contained a medicinal dose of the oil. The methylated spirit is purer than the dyed variety, and the castor oil may be separated roughly by adding water or milk and skimming off the oil. D. HENVILLE

CITY OF BIRMINGHAM

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1934

OF the 5383 samples submitted under the Sale of Food and Drugs (Adulteration) Act, 5092 were taken informally.

ASPIRIN TABLETS.—One sample, of the eleven examined, contained 2 per cent. of free salicylic acid and more than 6 per cent. of French chalk. Most aspirin tablets contain no insoluble mineral matter, and it seems unnecessary to incorporate any such material in tablets of this kind.

GRAPE FRUIT BUTTER.—Two samples contained only 2·5 per cent. of butter, the remainder consisting mainly of starch and sugar. In appearance and taste the article resembled lemon cheese, but was inferior, since an average lemon cheese contains 10 to 15 per cent. of butter. The use of the word "butter" as part of the description of this article appeared to be misleading and unjustifiable.

"DIGESTIVE" TEA.—It was claimed for a sample of tea that "It contains the essential goodness of the tea without any injurious tannin." Analyses showed that 13·9 per cent. of tannin was present. The packers were cautioned and agreed to withdraw the statement. The label on another sample (China tea) described it as "Practically free from tannin," whereas it contained 8·6 per cent., a normal figure for China tea. The claims of these so-called "digestive" teas are based on the supposition that all, or most, of the tannin is present, not in the free state, but combined with caffeine. Caffeine tannate is supposed to have less deleterious effects on the digestion than has tannin. So far as I am aware, there is no evidence that this supposition is correct, and it is extremely probable that even if tannin exists as caffeine tannate in tea infusions, the combination is split up on reaching the stomach, so that the characteristic physiological effect of tannin is produced whatever the original state of combination.

H. H. BAGNALL

Ministry of Agriculture and Fisheries

VARIATIONS IN THE COMPOSITION OF MILK*

THE first edition of this Bulletin was issued as the outcome of a conference, in 1927, between experts in dairy chemistry and officials of the Ministry of Agriculture and of the Board of Agriculture for Scotland. The present, second, edition has been revised and extended in consultation with members of the staff of the National Institute for Research in Dairying.

Vitamin Standards

WE have been asked by the Director of the Department of Biological Standards, National Institute for Medical Research, to publish the following statement:

At the request of the Health Organisation of the League of Nations, the Board of Trustees of the United States Pharmacopoeia have kindly consented to make generally available the standard cod-liver oils, prepared for use in the United States as secondary standards for vitamins *A* and *D*.

The distribution of these oils will not be made through the National Distributing Centres as in the case of the Primary Vitamin Standards, but direct to individual users. They may be obtained from:—E. Fullerton Cook, Ph.M. (Chairman of the Committee of Revision of the U.S. Pharmacopoeia), 43rd Street and Woodland Avenue, Philadelphia, Pa., U.S.A. It should be clearly stated whether Vitamin *A* oil or Vitamin *D* oil is required. A charge of 2·50 dollars is made for containers holding 30 c.c.

A sum to cover the cost of the quantity required should be sent by International Money Order with the application. The oils will be sent post-free to their destinations.

These reference oils are checked each six months biologically against the International Standards by at least six laboratories, and their potency should therefore be increasingly dependable.

Fiscal Policy Joint Committee, Brass, Copper and Nickel Silver Industries

DETERMINATION OF BISMUTH IN COPPER

IN 1932 the Imperial proceedings at Ottawa directed attention to the question of a fuller use of the Empire's resources in raw copper. There was, however, a suspicion that some Empire brands contained proportions of bismuth which, minute though they were, would militate against the free use of such copper for certain purposes. Accordingly a Technical Sub-Committee was appointed to study the question and to explore the principles of analysis to be employed. As a result, in May, 1933, there was issued to individuals and to scientific journals a paper on the Determination of Small Proportions of Bismuth in Copper (up to 0·02 per cent.).

This paper attracted attention, and the Chemical Sub-Committee received, from many sources, helpful comments, which were studied and tested by the Committee. The following procedure, which embodies the methods of Allport and Skrimshire (ANALYST, 1932, 57, 440) and of Haddock (ANALYST, 1934, 59, 163),

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* Bull. No. 16. 2nd Ed. 1935. H.M. Stationery Office. Pp. 22. Price 6d. net (postage extra).

is now put forward. The effect of various impurities on the method has been studied, and it has been found that, whilst silver, nickel, arsenic and phosphorus do not interfere, the presence of small amounts of tin and lead necessitates certain modifications, which are incorporated in the method.

NEW RAPID METHOD SUITABLE FOR THE DETERMINATION OF BISMUTH IN COPPER IN QUANTITIES OF 0·0002 TO 0·005 PER CENT.*

Dissolve 2 g. of drillings in 20 ml. of 50 per cent. nitric acid in a 250-ml. flask or beaker (if any insoluble matter is present, proceed as directed in Note i). Evaporate the solution until it is viscous and brown fumes are evolved; then add 3 ml. of sulphuric acid (sp.gr. 1·84) and continue the evaporation until the nitrates are decomposed and white fumes of sulphuric anhydride are freely evolved. Allow the residue to cool, take up with 30 ml. of distilled water, add 1 g. of citric acid dissolved in 20 ml. of water, and render slightly ammoniacal with ammonia (sp.gr. 0·880), sufficient being added to take the copper salts into solution (from 12 to 15 ml. are usually required). Cool the solution and add to it, in the cold, 50 ml. of a freshly prepared 20 per cent. solution of potassium cyanide. Transfer the pale yellow solution to a short-stemmed 250-ml. separator; make up to 200 ml. with water and extract the bismuth by shaking well with successive 10 ml. volumes of a 0·1 per cent. solution of diphenylthiocarbazone in chloroform (see Note ii). Run off the chloroformic extract (*almost* all) into a 150-ml. separator; treat the ammoniacal aqueous layer with a further 10 ml. of a 0·1 per cent. solution of diphenylthiocarbazone in chloroform and repeat the extraction as before. Run off almost the whole of the third extract and shake the ammoniacal aqueous layer with 5 ml. of chloroform. Run the chloroform layer into the combined extracts and wash *thoroughly* with 50 ml. of distilled water. Transfer the washed extract to a 150-ml. flask or beaker, and evaporate off the bulk of the chloroform, taking care that the evaporation is *not* continued to dryness. Mix the organic residue with 1 ml. of sulphuric acid (sp.gr. 1·84), heat until white fumes are freely evolved, cool slightly, add cautiously 2 to 3 ml. of hydrogen peroxide (20 vols.), and continue the evaporation until white fumes are again evolved and the liquid is colourless (see Note iii). Allow the solution to cool, dilute with 15 ml. of distilled water, and filter off any precipitated lead sulphate (see Note iv). Transfer the solution to a 50-ml. Nessler glass, add 10 ml. of a 2 per cent. potassium iodide solution and then sulphurous acid (1 in 10), drop by drop, until any free iodine colour is discharged; add one drop in excess, and make up the volume to 30 ml. (see Note v). Prepare a blank solution in a second Nessler glass by adding 10 ml. sulphuric acid (1 in 10), 5 ml. distilled water, and volumes of reagents similar to those used in the assay solution. Standard bismuth solution is added to the blank solution until the colours in the Nessler glasses are identical (see Note vi). The time required for the determination is from 1½ to 2 hours.

NOTES

I. Any stannic hydroxide or other insoluble matter is to be filtered off, ignited and fused with potassium bisulphate. The fused mass is leached out with water, and the aqueous extract is combined with the original solution.

II. It has been found that three extractions are normally sufficient, but if the third extract is bright red in colour, it may be due to residual bismuth, or the presence of zinc or lead. These colour changes do not necessarily indicate that there is more bismuth to extract, but if any doubt exists as to whether the complete extraction has been effected, it is advisable to treat a fourth extract separately by wet oxidation and subsequent matching. The diphenylthiocarbazone solution is reliable for use for two or three weeks after preparation.

III. If the liquid is not colourless, completion of the wet oxidation by further addition of hydrogen peroxide, with subsequent fuming, is necessary.

IV. If a precipitate of lead sulphate is produced, it is to be filtered off, ignited and dissolved in 10 ml. of hot hydrochloric acid (sp.gr. 1·18). To the cooled solution add 1 g. of tartaric acid, 1 ml. of nitric acid (sp.gr. 1·42) and 1 ml. of sulphuric acid (sp.gr. 1·84), and evaporate to complete the expulsion of the more volatile acids. The point at which the nitric and hydrochloric acids are driven off is marked by the cessation of red fumes and the sudden quiescence of the mixture. Take up with 15 ml. of water, filter, and combine the filtrate with the solution to be matched by colorimetric methods. In this case, take care to regulate the concentration of acid and volume of liquid in both the assay and blank solutions.

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* The Chemical Sub-Committee will be pleased to receive comments from any who are interested, and these should be addressed to J. Lester Smith, Kings Court, 115, Colmore Row, Birmingham (Eng.), Secretary to the Committee.

V. An alternative method, by Haddock, is as follows: To the solution in the Nessler glass add a slight excess of $N/100$ iodine solution, drop by drop, destroy the excess of iodine by the addition of 4 to 6 drops of sulphurous acid solution (1 in 20), add 2 ml. of a 30 per cent. solution of hypophosphorous acid and 10 ml. of a freshly prepared 2 per cent. solution of potassium iodide, and make up the volume to 30 ml.

VI. The standard bismuth solution is prepared by dissolving 0·05 g. of metallic bismuth in 10 ml. of sulphuric acid (sp.gr. 1·84) and making up to 1 l. (1 ml. = 0·00005 g. of bismuth). The colours may be conveniently matched by the use of a simple colorimeter as described by Rowell (*J.S.C.I.*, 1908, **27**, 102). In the absence of a colorimeter, an alternative method is to prepare a series of standard solutions containing different amounts of bismuth solution in which the reagents have been added in the same order as in the assay solution. If the assay solution under test requires more than 2·0 ml. of the standard bismuth solution, it is advisable to make up to known bulk the solution so obtained, and to take an aliquot portion for the final colour matching procedure.

Appendix

I. If fine drillings are available, they may be dissolved in a mixture of 20 ml. of hydrochloric acid (5 N) and 2 g. of potassium chlorate, and the excess chlorine removed by boiling. This procedure eliminates the need for "fuming" with sulphuric acid to ensure complete decomposition of all nitrates.

II. It is emphasised that the conditions stated should be strictly adhered to, the described method and quantities being satisfactory for the determination of 0·0002 to 0·005 per cent. bismuth. *For quantities below 0·0002 per cent. and above 0·005 per cent. the initial weight of sample taken must be amended, and be accompanied by an equivalent alteration in the quantity of reagents used.* An alternative procedure is to dissolve a larger weight of the sample in nitric acid, make the solution up to known bulk, and take an aliquot portion (equivalent to 2·0 g. of sample) for the determination.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Variations in the *p*H Value during the Souring of Milk. S. N. Mayoroff. (*Z. Unters. Lebensm.*, 1935, **69**, 301–305.)—Although the variations in the acidity of milk are quite large, ranging from 15 to 21 degrees, and even more in individual instances, the *p*H value, according to Inichoff (*Biochemie der Milch*, 1933), is moderately constant, and can probably serve as a means of determining its quality. Since milk is a complex mixture containing several buffer systems a correspondence between acidity and *p*H value is not to be expected. Divergent views are held concerning the change of *p*H value during spontaneous souring. Sharp and McInnerney (*J. Biol. Chem.*, 1927, **75**, 177; Abst., ANALYST, 1927, **52**, 715) assert that a constant ratio exists between the *p*H value and the acidity, and that it is possible to calculate the *p*H value with an accuracy of ±0·06. Grimmer and Arlart (*Milchw. Forsch.*, 1930, **9**, 100) give a method of calculating *p*H value from acidity, the *p*H varying as the square of the acidity on the Soxhlet-Henkel scale. Tillmans and Obermeier (*Z. Unters. Lebensm.*, 1920, **40**, 23) and van Slyke find no constant relation, and van Slyke suggests that the *p*H depends upon the species of bacteria causing the souring. Inichoff states that up to an acidity of 22° the *p*H value is fairly constant. If the *p*H value of milk changes, it is a certain sign that the milk has been damaged. Henneberg states that a whole series of bacteria, which can cause the decomposition of milk albumin into ammonia and other substances, can produce an alkaline reaction, resulting in alteration of taste and loss of value. Moreover, in certain udder diseases, the *p*H value shows strong deviations from the normal. In the present investigation the *p*H value was determined by means of a concentration cell with a hydrogen electrode. Six samples were taken from each of four cows. These, after the morning milking at 4 to 5 a.m., were placed in clean vessels at 20 to 25° C. The *p*H values and the acidities were determined at 8 a.m., 2 p.m. and 8 p.m. From the results it appears that during storage the acidity increases steadily, whilst the *p*H value varies irregularly. In about 50 per cent. of the experiments during the period between the first and second test an increase in the *p*H occurred, being brought about by the decomposition of albumin with the formation of alkaline products. Since casein contains about 15 per cent. of lysine, arginine and histidine, the separation of these bodies may raise the *p*H value without influencing the titration value.

Morres has suggested the degree of curdling as a criterion of the quality of the milk. This is the sum of the acidity (Thörner scale) and the ml. of 0·1 *N* sulphuric acid that must be added to curdle the casein. Morres gives the value for normal milk as not below 62. The determination of the curdling-point presents some difficulty when the coagulation does not form immediately on the addition of acid and when a fine turbidity results, more acid being required to produce a definite deposit. Lebermann (*Biochem. Z.*, 1929, **206**, 56) mixed skim-milk with an acetate buffer solution (*p*H 4·62) in the ratio 1 : 1, and a small amount of casein separated out. On allowing spontaneous souring to proceed, a strong deposit of casein was formed in two days. He found the optimum condition for the separation of casein to be a mixture of 1 part of milk with 8 parts of the buffer solution, the *p*H value being 3·74, *i.e.* well above the limiting value for casein precipitation, *viz.* 4·7. According to van Slyke only 86 to 87 per cent. of the casein in curdled milk exists in the free state, the remainder being in solution as monocalcium caseinate. Tapernoux, Armand and Katrandjieff (*Compt. rend. Biol.*, 1929, **101**, 828) state that casein coagulation is a function of the *p*H value and the temperature. The titration by the method of Morres will not give correct results if a decomposition of albumin, with the production of basic bodies, occurs side by side with the acid fermentation of the lactose. The critical coagulation-point, depending as it does upon different conditions, cannot be regarded as having a constant value. Also, it can only be useful as a criterion for the milk of large herds; in individual cows it may vary from 40 to 149. Inichoff (*loc. cit.*) has applied the method in a large number of tests of herd milk, and suggests 55 as the normal figure. He states that the lactation period has an influence upon the degree of coagulation, and that on the average the variation in this respect is from 42·3 to 68·4. Recorded results in this investigation show that in some instances an increase in the *p*H value is accompanied by a lowering of the coagulation-point, although there is no definite relation between the two values. From the hygienic standpoint this indicates that the condition of the milk is bad. It is probable that after further investigations a method will be found of employing the *p*H value as a criterion of the quality of milk. A. O. J.

Formol Titration Number as a Means of Evaluating Fruit Juices, Fruit-Lemonade Syrups, Jams and Wines. W. Schut. (*Chem. Weekblad*, **1935, 32, 371–373.**)—With coloured samples the following method (adapted from that of J. Tillmans and J. Kiesgen, Abst., ANALYST, 1927, 52, 417) is recommended:—The acidity is first determined by titrating a mixture of 10 ml. of the sample and 100 ml. of water with 0·5 or 0·1 *N* sodium hydroxide solution (phenolphthalein as indicator). When the end-point is near, a portion of the liquid is placed in a test-tube, and the colour is viewed vertically through the column of liquid. This is repeated after each addition of 2 drops of alkali, and the end-point may thus be observed with an accuracy of approx. 0·1 ml. The portion of the solution at the end-point may be used as a standard for the formol titration, which is then carried out by adding 30 ml. of a 30 per cent. solution of formalin and again titrating with 0·1 *N* sodium hydroxide solution to the same colour and in the same way (accuracy 0·1 ml.). The formol value (*C*) is expressed as the number of ml. of the *N* alkali per 100 ml. of the sample, and data are given for a large number of different fruit juices (prepared by the author) and for fruit conserves, jams and wines; these include the ratios ash : alkalinity of the ash, and alkalinity of the ash : *C*. There appears to be no useful relationship between *C* or these values and the nature of the fruit in the case of pure fruit juices, but the values of *C* obtained for fruit lemonade syrups are considered to be useful as an aid to evaluation, and are as follows:—Cherry, 0·2 and 0·6; pineapple, 0·1; lemon, 0·4; raspberry, 0·6; orange, 0·1 to 1·7. Mean values for 36 grape wines and 30 fruit wines were:—Champagne, 0·45; port, 0·51; red wine, 0·87; white wine, 0·41; tokay, 1·14; red and white currant wines, 0·07; gooseberry, 0·13; apple, 0·06; raspberry, 0·1; cherry, 0·1; various fruit wines of unknown composition, 0·16. It is therefore possible to distinguish the grape wines from fruit wines (mean values 0·60 and 0·08, respectively). J. G.

New Reaction of Tartaric Acid. M. Pesez. (*J. Pharm. Chim.*, 1935, **127**, 542–546.)—The well-known reaction of Denigès for tartaric acid, which depends upon the condensation of the products of decomposition of tartaric acid in hot sulphuric acid with resorcinol, though sensitive, is not conclusive when the reaction gives a negative result. According to Denigès (*Bull. Soc. Pharm. Bordeaux*, 1895, 161), the presence of chromates and permanganates, nitrites, nitrates and chlorates affects the interpretation of the reaction. These substances can be removed by means of a zinc-copper couple. In the present investigation it was found that, in addition to the substances mentioned above, the per-salts of iron, and bromates, bromides, iodates and iodides produce abnormal results. Reduction with zinc converts the ferric salts into ferrous salts, and the bromates and iodates into bromides and iodides, with the possible liberation of bromine or iodine, which will render observation impossible. Particularly in the presence of bromides, and at a certain concentration, an intense blue colour is produced. This suggests a new modification of Denigès' reaction:—The resorcinol reagent is replaced by a solution containing 2 g. of resorcinol and 10 g. of potassium bromide in 100 ml. of distilled water. After solution, 1 ml. of sulphuric acid is added. This solution keeps well if stored in brown flasks with ground-in glass stoppers. Two ml. of sulphuric acid (sp.gr. 1·84) are mixed with 0·1 ml. of the reagent and 0·1 ml. of a solution of tartaric acid in a test-tube, which is placed in a water-bath. In a few minutes a deep blue colour is produced, and on cautiously adding 1 ml. of water, the colour changes to a "gooseberry red," and this colour does not disappear on the addition of 10 ml. of water. If the solution is then neutralised, a rather fugitive violet colour is observed. The reaction does not take place if the reagent is replaced by a solution of tribromoresorcinol; only the violet colour of the reaction of Denigès is then produced. It appears, therefore, that nascent bromine is essential to the reaction. With 0·0001 g. of tartaric acid a very clear pale blue colour is produced. With this amount the course of the usual reaction is obscured by the charring action of the sulphuric acid. Several other substances reacting as phenols were tried in the place of resorcinol, but the blue colour appears to be specific for this substance, and the reaction may therefore serve for the detection of resorcinol. The substitution of oxalic, benzoic, salicylic, uric, lactic and citric acids, antipyrine, chloroform, ethanol, methanol, glycerin or its oxidation products, for tartaric acid did not produce any indication of the blue colour. Chloral, however, gives a positive reaction, and must therefore be removed by warming with sodium hydroxide before making the test. In the presence of bromates, nitrites and ferric salts the reaction is still positive. It is negative with hypochlorites, chlorates, nitrates, permanganates, iodides, iodates and chromates. The removal of hypochlorites, chlorates, nitrates and permanganates can be effected by reduction with a zinc-copper couple. With iodates the reduction causes liberation of iodine and, after filtration, a slightly yellow solution is obtained which gives a positive reaction. The sensitivity of the reaction is such that the green colour produced by the reduction of chromates may be counteracted by high dilution. Iodides may be removed by addition of silver nitrate, the nitrate ion being subsequently reduced by a zinc-copper couple. A. O. J.

Iodine in Cabbage. J. F. McClendon and C. E. Holdridge. (*Biochem. J.*, 1935, 29, 272–274.)—The determination of the proportion of iodine in cabbage leaves depends chiefly on the careful destruction of the organic material without loss of iodine, and, in order to ensure this, weighed samples of the sliced, ground and dried leaves were placed in Visking sausage casing and burned in a modified combustion tube (illustrated), at normal or slightly reduced pressure. In the east-north-east section of Minnesota cabbages from 14, and potatoes from 9, counties were examined, and data on goitre were available from 37 counties. The average iodine-content of cabbage was 111γ per kg. of dry material, that of potatoes 101γ, and the goitre figure per 1000 men was 17·2; in the west-south district the iodine-content averaged in cabbage 174γ, and in potato 227γ per kg., and the goitre figure was 8·5. Goitre is thus associated with iodine deficiency in the foodstuffs eaten as well as in the water consumed (*cf. Biochem. J.*, 1934, 28, 304).

D. G. H.

Compound Glycerides of Hen Body-Fats. T. P. Hilditch and W. J. Stainsby. (*Biochem. J.*, 1935, 29, 599–605.)—The compound fatty acids of hen body-fat have already been discussed (ANALYST, 1934, 59, 707), and the present work has been carried out to ascertain the proportion and value of the fully-saturated glycerides in the original fat; to fractionally crystallise completely hydrogenated hen body-fat, and to make a complete analysis of the fat after hydrogenation to a point (iodine value 14·6) at which by analogy with pig depôt fat all di-palmito glycerides will have passed into the fully-saturated portion; and to fractionate by crystallisation these fully-saturated glycerides. The chief glycerides studied in hen body-fat are the mono-palmito-di-"oleins," about 40 per cent. (mol.), with nearly 30 per cent. (mol.) each of mainly unsaturated tri-C_{18}-glycerides and of di-C_{16} mono-C_{18}-glycerides, and the fully-saturated glycerides (mainly tripalmitin) form only about 2 per cent. of the fat. The combined stearic acid (approx. 7 per cent.) may be present in the form of mono-stearo-glycerides in either of the 3 main groups, the combined amount approximating to 20 per cent. (mol.) of the fat. Oleic and linolic acids are present to the amounts of about 36 and 21 per cent., respectively, of the component acids, but their distribution cannot be given, since the glyceride structure is deduced from a study of the fat after hydrogenation. The mono-palmito glycerides appear to be present as palmito-di-"oleins" (or in part as palmito-stearo-"oleins"), whilst the di C_{16}-glycerides consist chiefly of palmito derivatives, and this group probably includes the 8 per cent. of palmitoleic acid in hen fat. On this basis the di-C_{16}-glycerides may be α-palmito-β-palmitoleo-α'-"olein," α-palmito-β-"oleo"-α'-palmitolein, α-palmito-β-palmitoleo-α'-stearin, or a mixture of these. The unusually large proportions of tri-C_{18} (unsaturated) glycerides, and especially of the mixed semi-unsaturated di-C_{16}-mono C_{18} glycerides distinguish hen fat from the corresponding pig, sheep, and cow fats, and the mixture is of a more heterogenous type than is found in the lard type. This is brought out in the fact that at atmospheric temperature hen body-fat separates into a clear liquid fat with a lower layer of solid glycerides, whilst a pig fat of similar mean unsaturation forms a thin, semi-solid, almost homogeneous paste.

D. G. H.

Colour Reaction of Pyramidone. N. Schoorl. (*Pharm. Weekblad.*, 1935, **72**, 669–670.)—Wagenaar (*cf. id.*, 1935, **72**, 564, and abstract, p. 575) has found that a weak oxidising agent, such as a 5 per cent. solution of potassium persulphate, produces a blue or purple oxidation product with pyramidone, and that this may be used as a test in the presence of antipyrine, which does not react. Schoorl states that 0·1 *N* iodine solution is preferable. Thus addition of 1 drop to 5 ml. of a 0·01 per cent. solution of pyramidone gives a positive result, whereas potassium persulphate does not react. The colour is also produced more rapidly with iodine, and is more stable.

J. G.

Distinction of Chloroform and Carbon Tetrachloride. J. Rozeboom. (*Pharm. Weekblad*, 1935, **72**, 689.)—In 1 ml. of sample (from which alcohol must be absent) is dissolved a small crystal of iodine and 10 mg. of papaverine hydrochloride (or of any other salt which is soluble in chloroform but not in carbon tetrachloride, *cf.* ANALYST, 1935, 482) are added. If, when shaken, the mixture turns from violet to yellow-red and becomes brighter, chloroform is present; with carbon tetrachloride there is no appreciable change.

J. G.

Sucrose Octa-Acetate as a Compulsory Denaturant for Rubbing Alcohol. Anon. (*Perfumery and Essential Oil Record*, 1935, **26**, 180–182.)—As from 1st June, 1935, the following formula (No. 23-G) for specially-denatured alcohol for rubbing compounds has been authorised by the Bureau of Internal Revenue, Washington:—Ethyl alcohol, 100 gallons (Amer.); acetone, U.S.P., 10 gallons (Amer.); sucrose octa-acetate, 4·25 lbs. (avoir.). Sucrose octa-acetate is a white non-hygroscopic powder having a very bitter taste, and it should conform to the following specification (T.D. 4541):—The m.p. should not be below 69·0 or above 72·0 C. If 1 g. of the sample is boiled under a reflux condenser for 10 minutes in the presence of 100 ml. of water and 1·5 ml. of conc. hydrochloric acid, and 10 ml. of the resulting solution are heated in boiling water with 10 ml. of Benedict's solution for 10 minutes, a red precipitate should be produced. The free acidity, as acetic acid, should not exceed 0·15 per cent. by wt. when determined by titration of a solution of 1 g. of sample in 50 ml. of neutral alcohol, to phenolphthalein, with 0·1 N sodium hydroxide solution. The sucrose octa-acetate content (which should not be less than 98·00 per cent. by wt.) is determined by adding a known weight (x, approx. 1·5 g.) of the sample to a mixture of 100 ml. of neutral ethyl alcohol and 50 ml. of 0·5 N sodium hydroxide solution; the mixture is boiled under a reflux condenser for 1 hour, and then cooled and back-titrated (phenolphthalein as indicator) with 0·5 N sulphuric acid (y ml.). Then $8{\cdot}48\,(50 \times 0{\cdot}5 - 0{\cdot}5\,y)/x$ gives the percentage of sucrose octa-acetate. The insoluble matter should not exceed 0·30 per cent. Rubbing alcohols must contain, as nearly as possible, 70 per cent. by vol. of absolute ethyl alcohol, and therefore 103·7 fluid ounces of the above denatured alcohol (No. 23-G) should be added to any two of the following ingredients in the quantities indicated, and the mixture then made up to 1 gallon with water:—Zinc sulphocarbolate, U.S.P. IX, 512 grains; boric acid, U.S.P. X, 640 grains; tincture of quassia, U.S.P. IX, 256 minims; diethyl phthalate (not less than 99 per cent.), 1·28 fluid ounces. Other regulations regarding the manufacture and sale of these solutions are given. J. G.

Biochemical

Copper Metabolism in Man. Tung-pi Chou and W. H. Adolph. (*Biochem. J.*, 1935, **29**, 476–479.)—Copper-balance experiments were carried out on 3 Chinese subjects who were given a low copper diet of steamed bread, milk and vegetables. The balance was determined on a subject daily for 4 successive days to find how rapidly the body adjusted itself to altered copper-intake; then 3 subjects consumed prescribed diets of increasing copper-content over 4 periods, each period of 4 to 6 days, and following each other without a break. It was found that equilibrium was reached when the copper-intake was about 2 mg. a day. Copper excretion is mainly by the faeces; that excreted in the urine does not vary appreciably with varied copper-intake and averages 0·25 mg. a day. The copper-content in material from 5 cadavers, including those of 2 adults, was determined, and the total average amounts found in the various parts was estimated in mg. as: heart, 1·5; liver, 18·0; kidney, 0·7; pancreas, 0·4; spleen, 0·4; lungs, 2·9; muscle, 63·6; bone, 23·4; and blood, 5·0. The total copper to be found in the whole body is probably between 100 and 150 mg. Copper appears to be associated with iron in haemoglobin formation, and the ratio of iron requirement (15 mg. per day) to copper (2 mg. per day) is almost identical with that worked out for the white rat, on the basis of haemoglobin-recovery experiments. D. G. H.

Substitution of Glycerides by the Corresponding Fatty Acids in a Balanced Ration. R. Lecoq. (*Compt. rend.*, 1935, **200**, 1979–1980.)—Experiments were conducted on six groups of 12 pigeons, each group being subdivided into 3 series of 4 animals, and the ration was administered at the rate of 15 g. a day. It was found that it was not possible to substitute the glycerides of a suitable diet by the corresponding fatty acids without upsetting the balance and producing in the pigeons polyneuritic symptoms followed by death, in spite of heavy additions of vitamin *B* in the form of yeast. Although in the presence of vitamin *B* such oils as arachis, linseed, palm, cod-liver, lard, cocoa butter and coconut oil can be used in the pigeons' ration to the extent of 50 per cent., castor oil cannot; neither can its fatty acids, nor does the addition of 10 per cent. of glycerol modify the action of the castor oil. The addition of glycerol in the presence of vitamin *B* to the fatty acids of olive oil does, however, diminish the action of the acids and prolongs the life of the animal, but, whatever the proportion of fatty acids present, their upsetting effect remains. It appears that glycerol in juxtaposition with the fatty acids cannot take the place of these two substances in combination as glycerides. Possibly some essential substance is removed during the course of extraction of the acids by saponification. D. G. H.

New Method for the Determination of Fructose in Blood. L. B. Scott. (*Biochem. J.*, 1935, **29**, 1012–1016.)—The amount of fructose in blood may be determined by a method based on the reaction between that substance and bile salts. The sensitivity of the method is of the order of ± 1 mg. when the fructose-content is 5 to 20 mg. per 100 ml. of blood. In a boiling-tube (25 × 150 mm.), graduated at 40 ml., 5 ml. of whole venous blood are placed. To this are added 30 ml. of water, followed by 5 ml. of 10 per cent. zinc sulphate solution and 5 ml. of 0·5 *N* sodium hydroxide solution, with thorough mixing after the addition of each solution. The mixture is then diluted with water to the 40-ml. mark and mixed thoroughly, and the tube is placed in a water-bath at 80 to 85° C. for 5 minutes, the water-level in the bath being kept above that of the solution in the tube. After 5 minutes the tube is cooled in running water and its contents again well mixed. The mixture is filtered through a No. 41, 9-cm. paper, the remaining gelatinous precipitate being stirred on the filter-paper to free the last few ml. of the filtrate. In a monax boiling-tube are placed 20 ml. of the clear filtrate, 0·15 ml. of 1 per cent. acetic acid solution are added, with a few pieces of silica to prevent bumping. This solution is then boiled down to a volume of about 1·5 ml. When the volume decreases, excessive heat must be avoided or charring will occur. The standard fructose tube is prepared by adding 2·5 ml. of a 0·01 per cent. fructose solution (made by dilution of a 1 per cent. stock solution) to another monax boiling-tube. The excess of water is carefully boiled off until the volume is about 1·5 ml. To both tubes 3 ml. of 2·25 per cent. alcoholic solution of sodium tauroglycocholate are added. After the addition of 7 to 10 ml. of absolute alcohol, a few more pieces of silica are added, and the contents of each tube are evaporated to dryness on a water-bath. If bumping occurs the blood-filtrate tube should be gently rotated until all the alcohol has evaporated. After the last drops of alcohol have disappeared the tubes are allowed to remain in the water-bath for an extra minute or two to ensure the complete removal of the last traces of alcohol, which should be accomplished without causing the precipitate to adhere too firmly to the bottom and sides of the tube. When cool, 10 ml. of concentrated hydrochloric acid are added to both tubes, which, after being shaken, are securely stoppered, and placed in a water-bath at 40° C. for half an hour, with occasional agitation to ensure an even emulsion and production of colour. A reddish-purple colour, proportional to the amount of fructose present, slowly develops, reaching a maximum intensity in thirty minutes. The tubes are removed from the bath and cooled in running water, and the solutions are filtered through No. 50, 7-cm. papers, the first 2 or 3 ml., which are slightly cloudy, being refiltered. The solutions are then compared in a colorimeter in the usual way.

If it is not possible to obtain venous blood, the test may be carried out on 2 ml. of whole blood (obtained by finger puncture) by the following modification:—Into a test-tube, graduated at 20 ml., 10 ml. of water, 2 ml. of blood and the corresponding amounts of precipitating agents are introduced. After dilution of the mixture to 20 ml. with water, the tubes are placed in the water-bath at 80° C. for five minutes. They are then cooled, and the solutions are filtered through a No. 41, 9-cm. paper. Into a monax tube, 10 ml. of the filtrate are measured, 2 drops of 1 per cent. acetic acid solution are added, and the mixture is boiled down to 1 ml. After the addition of 1 ml. of alcoholic bile salt solution and 7 to 10 ml. of alcohol, the mixture is evaporated to dryness in a boiling water-bath. The standard is prepared by mixing 1 ml. of a 1 in 100 dilution of the 1 per cent. fructose solution with 1 ml. of bile salt solution and 7 to 10 ml. of alcohol, and evaporating the mixture to dryness. Five ml. of concentrated hydrochloric acid are added to each tube, and both tubes are heated to 40° C. for 30 minutes. After cooling, the liquids are filtered through No. 50, 7-cm. papers, and the colours are compared as before. S. G. S.

New Method of Determining the Vitamin *A* Content of Blood. E. Rosenthal and C. Szilard. (*Biochem. J.*, 1935, 29, 1039–1042.)—The vitamin *A* content in blood may be determined without removing the carotene (if the amount of this is below 5γ in 1 ml. of the extract), by extracting 10 to 30 ml. of blood four times with 50 ml. of petroleum spirit (b.p. $< 55°$). The greater the quantity and the lower the specific gravity of the petroleum, the more easily is emulsification avoided. Should emulsification occur, the fluid may be treated with a few ml. of petroleum and centrifuged at low speed for 3 to 4 minutes. The addition of one drop of 96 per cent. alcohol may also break down an emulsion, but if this is used, the petroleum extract must be thoroughly washed twice with distilled water. The mixed petroleum extracts are dried over a minimum amount (0·01 to 0·02 g.) of anhydrous sodium sulphate for 2 hours, repeatedly filtered through dry filters, and evaporated *in vacuo* at 40° C. In order to remove the last traces of water, the residue is dried once more for 20 to 30 minutes *in vacuo*. To the dry residue of the extract 0·25 ml. of absolute chloroform, 0·25 ml. of 5 per cent. guaiacol solution in absolute chloroform and 0·5 ml. of a saturated solution of antimony trichloride in absolute chloroform are added. The mixture is put into a water-bath at 55° C. for 1½ minutes exactly. During this time the initial blue colour changes to purplish-red. It would be preferable to compare this solution with that of a known amount of pure vitamin *A*; but a 0·001 per cent. solution of potassium permanganate or the "grey solution" of the Leitz absolute colorimeter may be used for comparison. Until it becomes possible to determine the absolute amount of vitamin *A* by this test, its expression in "grey units" is suggested for research purposes. S. G. S.

Vitamin *A*-Active Substances in Egg-Yolk. A. E. Gillam and I. M. Heilbron. (*Biochem. J.*, 1935, **29**, 1064–1067.)—The unsaponifiable matter of egg-yolk has been examined by chromatographic methods with spectroscopic control, with a view to elucidating its growth-promoting activity. By means of a phase-test, separation of the carotene from the xanthophyll, followed by the adsorption of the latter on calcium carbonate, vitamin *A* has been obtained free from carotenoids. This has been confirmed both by the characteristic absorption band at 328$m\mu$ and by the antimony trichloride test. Examination of the petroleum-phasic carotenoids revealed the presence of kryptoxanthin and β-carotene. The kryptoxanthin-content of egg-yolk may be increased by feeding the fowls on a diet rich in maize; but the final value for the content of this vitamin *A*-active carotenoid is only about 0·2 mg. per 100 g. of yolk. S. G. S.

Observations on the Absorption of Carotene and Vitamin *A*. J. C. Drummond, M. E. Bell and E. T. Palmer. (*Brit. Med. J.*, 1935, 1208–1210.)—The absorption of vitamin *A* and carotene has been studied in a patient suffering from a condition in which part of the contents of the thoracic duct was directed into the pleural cavities. An analysis of the fluid which was removed at intervals from the chest cavities allowed an approximate estimation to be made of the amount of vitamin *A* and carotene which was absorbed by way of the chyle. It was found that practically all the vitamin *A* was absorbed, but only a small amount of the carotene given orally could be accounted for in the chylous fluid. When the vitamin was administered as the free alcohol, it was found mainly in the esterified condition in the lymph, and this linkage with fatty acids during its passage through the intestinal walls is thought to account for the high absorption coefficient of this substance as compared with carotene. Experiments with the chylous fluid showed that, when subjected to ultra-filtration at *p*H 6·5 to 8·0, or when dialysed at various reactions between *p*H 3 to 8, no trace of carotene or vitamin *A* was capable of passing through a collodion membrane. Both of these compounds appeared to be present in a colloidal form and to be closely associated with the highly dispersed fat globules. S. G. S.

Carotenoids of Butter. A. E. Gillam and I. M. Heilbron. (*Biochem. J.*, 1935, **29**, 834–836.)—The carotenoid fractions in the petrol phase of the unsaponifiable matter of normal and colostral butters have been examined both by chromatographic and spectroscopic methods. The carotene present in these butters is a mixture of α- and β-forms, but the ratio of α-: β-carotene varies from 9 : 1 to mainly β form only. The more pigmented samples of these butters were found to contain small amounts of lycopene and kryptoxanthin. S. G. S.

Potentiometric Titration of Solutions of Vitamin B_1. R. C. G. Moggridge and A. G. Ogston. (*Biochem. J.*, 1935, **29**, 866–870.)—Titrations at 18° C. and 0° C., using hydrogen and glass electrodes in aqueous solutions and glass electrodes in 90 per cent. ethyl alcohol solutions, have confirmed the form of curve obtained by Birch and Harris (*Thesis, Cambridge*, 1934). Crystalline vitamin B_1 hydrochloride was used, and the titrant solutions were $N/10$ in strength. The curves obtained indicate the presence of two weakly basic groups of *p*K 3·4 and 4·8. A pseudo-acid group which titrates about *p*H 9·0 is also present. The dissociation constant of the acid form of vitamin B_1 has the value *p*K 6·8 in water at 0° C. S. G. S.

Causes of the Instability of Vitamin *C* in Milk. J. E. Jacobsen. (*Z. Unters. Lebensm.*, 1935, **69**, 306–313.)—The method devised by Tillmans and his collaborators (*Z. Unters. Lebensm.*, 1932, **63**, 1, 21, 267, 276; Abst., ANALYST, 1932, **57**, 260, 396, 397) for the determination of vitamin *C* by reduction of 2·6-dichlorophenol-indophenol is applied to the investigation of the stability of vitamin *C* in milk. Experiments carried out both in acetic acid and acetate buffer solutions and in whey showed that, although ferrous ions are titrated easily at *p*H 5·5 to 6 and slowly at *p*H 3·1, they had practically no reducing action on the dye at *p*H 2·5. The solution of 2·6-dichlorophenol-indophenol was a 0·001 *N* solution in boiled water, which is stable for a week if stored in a cold place. It was prepared by rubbing about 0·078 g. of the dye with water in a mortar, decanting the clear liquid, and repeating the trituration with fresh water until about 200 ml. of solution had been obtained. The solution was standardised against freshly prepared lemon juice. Since the titration was carried out at *p*H 2·5, the addition of phosphate, as recommended by Tillmans, was not necessary. The serum prepared by Schlemmer's method (*i.e.* lead acetate followed by sodium sulphate) was not used since, although vitamin *C* is not precipitated, the serum loses its reducing power rapidly and also tends to become turbid on standing. Trichloroacetic acid cannot be used, as it interferes with the action of the dye. Acetic acid was found to give a satisfactory serum, and the separation was carried out as in the preparation of casein from milk, but the milk was diluted only to twice its original volume. A *p*H value of 2·5 is given by adding 1 ml. of *N* hydrochloric acid to 20 ml. of the serum. This amount of whey, corresponding with 10 ml. of the milk, is used for the titration. Its stability was increased by passing in carbon dioxide in a rapid stream both before precipitation and during filtration. The process is as follows:—A rapid stream of carbon dioxide is passed through 10 ml. of milk, acetic acid is added, and, after 10 minutes, the liquid is filtered while the stream of carbon dioxide is maintained, and finally the titration is carried out 5 minutes later. Exact adherence to these time intervals is not necessary. Experiments recorded show that the maximum value for the vitamin *C* content is obtained when carbon dioxide is passed in during the whole process, with the exception of the titration. Pasteurised and raw milks, the vitamin *C* content of which had been increased by the addition of lemon juice, showed a diminution of the vitamin *C* content with lapse of time when carbon dioxide was not passed through. After 10 minutes the serum loses about 10 per cent. of its reducing power, and in 70 minutes about 50 per cent. All the experiments recorded confirm the observation that the milk retained its reducing power because the addition of lemon juice was made while carbon dioxide was passing through. The influence of the presence of ferrous ions in the whey was also investigated. The iron salt was added in the proportion of 2 mg. of iron per l., partly to bring the iron-content near to that of human milk and partly in the hope that it would exert a beneficial effect on the stability of the vitamin. The results were not constant, but it was established that, with or without the addition of ferrous ions, the milk loses the greater part of its reducing power after the lapse of 24 hours at 20° C. Other conditions affecting adversely the retention of vitamin *C* activity were the storage of the milk in shallow layers of large surface area and the simple mixing to obtain average samples. The method of pasteurisation was found to have little effect on the reducing power. Since the rapidity of oxidation of vitamin *C* is influenced by catalysts, the effect of small amounts of nickel and copper salts was investigated. It was found that, although nickel had no catalytic action even at concentrations of 10 mg. per l., copper was strongly catalytic, even at concentrations of 0·1 mg. per l. This is important, as milk in its preparation for the market is liable to absorb traces of copper. The change from winter feeding to pasture exerts little effect on the vitamin *C* content. An adult can maintain his supply of vitamin *C* on 50 to 60 ml. of lemon juice. This is equivalent to about 3 l. of the best commercial milk. A. O. J.

Use of Pine-needle Concentrate to render Canned Preserves Antiscorbutic. N. Jarussowa. (*Z. Unters. Lebensm.*, 1935, 69, 381–383.)—Previous work (*Z. Unters. Lebensm.*, 1934, 68, 409) on the antiscorbutic properties of marmalade enriched by the addition of pine-needle concentrate is now extended to canned rice products. The method of preparation of these products is as follows:—Cold water is poured over boiled rice, the pasty mass is gradually introduced at 37 to 41° C. into the pine-needle concentrate in enamelled vessels, and the mass is thoroughly mixed, the whole process taking about 40 minutes. Aqueous sugar solution is then added, and the finished preserve will contain about 6 per cent. of the pine-needle concentrate. Within 15 to 20 minutes of its preparation it is filled into metal containers to within about 5 mm. of the lid. The cans are automatically closed and placed in an autoclave, the temperature of which is gradually raised to 112° C. in 20 minutes. After 90 minutes the heating is discontinued, the pressure released during the lapse of 15 minutes, and the cans are finally placed for 10 minutes in a vessel of water at room temperature.

In this investigation the action of the preserve has been tested for three different dosages, *viz.* 3, 9, and 13 g. of preserve containing 0·16, 0·48 and 0·7 g. of the concentrate, respectively. The prophylactic method was employed, each single dosage being administered to three guineapigs. All experimental animals receiving the dosage remained alive for 100 days, the standard time of the experiments. Details of the experiments are given. From the results obtained it appears that the lowest prophylactic dose of the preserve enriched with the concentrate, lies between 9 and 13 g.; hence 1 kg. of the product contains between 76 and 111 vitamin *C* units. As the daily requirement of vitamin *C* by human beings is about 20 units, the lowest prophylactic dose of the preserve lies between 180 and

260 g. The experimental preserve had, however, a bitter taste, and for general purposes a product containing a smaller amount of concentrate is preferable. A commercial product containing 1·7 per cent. of concentrate was found to be palatable. It is suggested that meat and fish products containing little or no vitamin *C* could be enriched by the addition of pine-needle concentrates and such products would be of value to the inhabitants of the arctic regions. A. O. J.

Organic

Testing of Acetone. E. S. Pemberton, S. T. Card and E. C. Craven. (*J. Soc. Chem. Ind.*, 1935, **54**, 163–167T.)—The published specification and tests for B.P. (1932), B.S.I. (1933, No. 509) and "Analar" (1934) products are described and discussed. *Identity and Acetone-Content.*—The B.P. nitroprusside test is criticised, since the 0·5 per cent. solution specified gives only a pale red colour, which becomes paler on dilution, instead of a deep red colour changing to violet; S. P. Mulliken ("Identification of Pure Organic Compounds," 1903) states that a 1 per cent. solution gives only a pale shade. Brady's 2:4-dinitrophenylhydrazine reagent (*J. Chem. Soc.*, 1931, 756) may also be used for identification. Messinger's iodoform method is unreliable except as a micro-reaction, when 5 p.p.m. may be determined nephelometrically in solutions saturated with sodium chloride, the error being less than 1 p.p.m. The best quantitative method is titration, with 0·5 *N* sodium hydroxide solution, of the acid liberated from *N*-hydroxylamine sulphate solution. The reaction is rapid, but not more than 75 per cent. of the reagent should be decomposed, and the result must be divided by a factor which is dependent on the degree of hydrolysis of the acetoxime at the *p*H value of the end-point (0·983 for methyl orange xylene cyanol, *p*H 3·7; and 0·988 for the "B.D.H. 4·5" indicator). Bromophenol blue and dimethyl yellow are not recommended (*cf. ibid.*, 1922, 2502; 1934, 323). *Sp.gr.*—Water is the only impurity, likely to be present in reasonably-good acetone, which will affect the sp.gr. The most reliable results are those given in the Landolt-Börnstein Tabellen (IIa, p. 290), but W. Young (*J. Soc. Chem. Ind.*, 1933, **52**, 450T) has found $d^{20°}$ of pure acetone to be 0·7905, and that small amounts of water raise it at the rate of 0·0030 for 1 per cent. *Distillation Range.*—Available b.p. data are discussed, and it is concluded that the b.p. 56·15 ± 0·05° C. may be accepted with confidence. The B.P. range (95 per cent. between 56° and 58° C.) is unnecessarily wide, and the B.S.I. and A.R. specifications require not less than 95 per cent. to distil between 55·5° and 56·5° C. In view of the difficulty of making accurate determinations of the true temperature it is suggested that 50 per cent. of the sample should distil at 56·15° C., the remainder of the readings being corrected accordingly. Water and methyl ethyl ketone produce very marked rises in distillation temperatures. *Water* (*cf.* Sp.gr., *supra*).—The best of the solutions investigated for miscibility tests was a mixture of 80 vols. of kerosene and 20 vols. of paraffin liquidum. A selected sample of acetone should be dried over calcium chloride until the temperature of separation ceases to fall (other drying agents form mesityl oxide or are not effective); the acetone is then distilled, and the critical solution temperatures are determined, after addition of up to about 1 per cent. of water, on mixtures containing 30 vols.

of hydrocarbon mixture and 70 vols. of sample. Data are given which show that the relation between water-content and separation-temperature is a linear one (17·0° C. for pure acetone, and 25·3° C. for 1·0 per cent. of water by wt.); up to 1 per cent. of ethyl alcohol has no effect on the temperatures. *Total Acidity* (*i.e.* acetic + carbon dioxide).—A mixture of 5 ml. of 0·01 *N* barium hydroxide solution, 50 ml. of sample and 50 ml. of water is boiled gently for 5 minutes, and is then cooled and titrated with 0·01 *N* acetic acid, with the B.S.I. phenolphthalein indicator; allowance is made for any blank titration. *Acetic Acidity.*—A mixture of 50 ml. of sample and 50 ml. of water is boiled for 5 minutes and cooled, and a convenient excess of barium hydroxide solution is added and back-titrated as before; allowance is again made for any blank, and the water used should have an acid- or alkali-requirement not exceeding 0·1 ml. of a 0·01 *N* solution. Since barium carbonate is much less soluble in mixtures of acetone and water than in acetone alone, the precipitation of this substance in the turbid state indicates the presence of carbon dioxide; quantities of the order of 0·0002 per cent. of acetic acid and 0·001 per cent. of carbon dioxide may be expected. *Alkalinity.*—The B.S.I. test is satisfactory; it responds to small quantities of ammonia, but not to bases such as aniline or pyridine. *Permanganate Test.*—The end-point is difficult in the B.S.I. method, and it is best to take the moment when the eye can no longer see any blue shade in good daylight, although it has been shown that reduction is then still incomplete. The importance of absence of light and of a fixed temperature during the test are emphasised; acetone will not withstand the test after exposure to sunlight or to a mercury vapour lamp (*cf.* K. Wiesler, *Z. angew. Chem.*, 1927, **40**, 1023). The B.P. statement, that the test gives the "limit for methyl alcohol and other readily oxidisable substances," is erroneous, as the test will not detect methyl or ethyl alcohol or formic acid. *Aldehydes.*—A mixture of 5 ml. of Tollens' reagent and 2 ml. of the sample develops a marked brown colour after 5 minutes in the presence of 0·01 per cent. of aldehyde, and quantities of this order may also be estimated by Schiff's reagent, if freshly-prepared standards are used. *Alcohol* (*cf. J. Soc. Chem. Ind.*, 1933, **52**, 239T).—A mixture of 1 ml. of sample and *x* ml. of Agulhon's reagent (a 0·5 per cent. solution of potassium dichromate in colourless nitric acid, sp.gr. 1·332) is allowed to react for 5 minutes, *x* being adjusted by trial and error, so that an end-point is obtained when determined by the method described by Craven (ANALYST, 1933, **68**, 776); 1 ml. of reagent ≡ 0·00117 g. of ethyl alcohol. The method is sensitive to methyl alcohol, higher alcohols and aldehydes, and in the form prescribed by the B.S.I. it will pass about 0·4 per cent. of alcohol.

J. G.

Some Characteristic Features of the Glycerides Present in Marine Animal Oils. T. P. Hilditch. (*Proc. 5th Pacific Science Congress. University of Toronto Press.* B.6.11.)—This paper collects together much of the work recently carried out on the glyceride structure of marine animal oils, and surveys the present position of knowledge. Marine animal oils share with the seed fats of members of the *Cruciferae* and *Umbelliferae* families (and certain marine algae) the peculiarity of containing a mixture of fatty acids entirely distinctive and made up to the extent of about 40 to 60 per cent. of unsaturated acids with other than

18 atoms of carbon in the molecule. Also, whilst those acids containing 16 carbon atoms or less are almost exclusively monoethylenic, those of the C_{20} and C_{22} series usually comprise not only monoethylenic, but also highly-unsaturated acids containing the equivalent of 3, 4, 5 and, perhaps, even 6 ethylenic linkings. The individual chemical structures of the various fatty acids are described, and the proportions in which they are found in the marine animal oils are given. The modern method of component-acid determination of dividing into solid and liquid acids by the solubility of the lead salts in alcohol, and the subsequent practice of conversion of each group into methyl esters and low-pressure fractionation is mentioned, and tables are given summarising the figures for the component acids of many marine animal oils. The technique whereby those glycerides which contain only saturated acid radicles can be quantitatively isolated from a fat is regarded as more particularly suited to the sperm whale oils among marine animal fats, but the selective crystallisation of the bromo addition products has been productive in establishing the presence of a sufficient number of mixed glycerides to justify the conclusion that the distribution of the component acids of a fish or whale oil among the glycerol molecules of the fat is profoundly heterogeneous, and that, whilst simple triglycerides are either absent or very rare, the most common form is a triglyceride containing three different acids, although sometimes two radicles of the same fatty acid are observed in a single molecule. At present the technique necessary for the quantitative or semi-quantitative analysis of these complex mixtures of unsaturated glycerides is not available, but when the methods become available, valuable generalisations correlating the details of glyceride structure in the particular fish or mammal are soon likely to be forthcoming. Already certain families are known to possess definite characteristics; *e.g.* the elasmobranch fish-liver oils show a relationship between the amount and nature of the unsaponifiable matter and the character of the component fatty acids. The liver oils of the *Gadidae* and the flesh oils of the three members of the herring family already examined show well-defined similarities in composition. The frequent occurrence in marine animal fats of the highly unsaturated acids of the "clupanodonic" group appears to be correlated with the presence of these acids in a large number of algae and plankton which serve as food for the fish. The sperm whale stands apart, in that the acids of the head oils are unique for animal oils, in the content of capric (3 per cent.), lauric (16 per cent.), and myristic (14 per cent.) acids, whilst palmitoleic acid forms, respectively, 15 per cent. and 26 per cent. of the acids of the head and blubber oils. D. G. H.

Iodine Value of Tung Oil. K. Ho, S. Wan and S. H. Wen. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 96.)—The iodine value of tung oil was determined under various conditions, and it was found that even after 12 days it still tended to increase. The statement that the iodine value is usually directly proportional to the percentage excess of Wijs solution, is found not to be strictly true, and only holds when the percentage excess is above 39. It is, however, proportional to the excess of iodine in centigrams of equivalent iodine per g. of oil, and if the Wijs solution added and the weight of oil are kept at a constant ratio, practically identical iodine values are found, temperature and time being kept the same. When time of contact and excess of iodine are kept constant the iodine value increases with increase of temperature. Similar iodine values may be obtained when the same excess of Wijs solution is used at different temperatures if the time of contact is varied according to the equation log H (in hours) = 0·030103 (20 — *t*). In order to convert experimentally obtained iodine values, within limits, to desired conditions, the following formula may be used:—$\log Yt - 0{\cdot}001672\ (t + 10{\cdot}56)\ (\log X - 2{\cdot}15) + 2^{(\frac{t}{10})} \times 0{\cdot}0008625 + B$. It is suggested that the standard conditions for obtaining the iodine value of tung oil should be: concentration of Wijs solution, 2·5 to 2·6 cg. of equivalent iodine per ml.; excess of iodine, 250 cg. of equivalent iodine per g. of oil; temperature 20° C.; time of contact 1 hour; and strength of reagents; potassium dichromate solution, 3·8635 g. in 1 l.; starch solution, 1 g. of soluble starch in 100 ml. of boiling water; sodium thiosulphate solution, 24·82 g. of the salt ($Na_2S_2O_3 5H_2O$) in 1 l., standardised after 1 month by the Volhard method. A simplified formula for converting the iodine value of tung oil for these proposed conditions is log Y = 0·0161 + B. D. G. H.

Highly Unsaturated Acids from Oiticica Oil (*Licania rigida*). **W. B. Brown and E. H. Farmer.** (*Biochem. J.*, 1935, **29**, 631–639.)—There are two forms of oiticica oil on the market. These come from Brazil, one being normally an oil and the other a solid of m.p. about 20° C. Various botanical derivations have been assigned to oiticica, *e.g. Couepia grandiflora*; *Moquilea tomentosa*; *Pleragina umbrosissima* and *Arruda camara*, but most recent opinion ascribes it to *Licania rigida*. On saponification, oiticica fat yields a solid triene acid, m.p. 74–75° C., whose constitution was adduced by analysis and synthesis as γ-keto-$\Delta^{\theta\kappa\mu}$-octadecatrienoic acid, $CH_3{\cdot}(CH_2)_3{\cdot}(CH:CH)_3{\cdot}(CH_2)_4{\cdot}CO{\cdot}(CH_2)_2{\cdot}CO_2H{\cdot}$, that is the same acid as is obtainable from the freshly extracted oil of *Licania rigida*, and the acid is now called licanic acid. The liquid oiticica oil appears to be a partly polymerised oil, for it has a high sp.gr. (0·9898) and low iodine value (108·2), and the acid obtained from it is another form of γ-keto-$\Delta^{\theta\kappa\mu}$-octadecatrienoic acid of m.p. 96·5° C.; it differs from its isomeride only in geometrical configuration and is designated *iso*-licanic acid. Probably this *iso*-licanic acid is all that remains of the original licanic acid, the rest having been oxidised, cyclised or polymerised. Oxidation of 37·5 g. of licanic acid by means of permanganate yielded eventually 12·6 g. of keto-azelaic acid, and investigation of the constitution of this acid showed it to be the γ-keto-compound. Licanic acid is regarded as the first naturally occurring ketonic unsaturated acid to be described, and is probably identical with the couepic acid of van Loon and Steger (*Rec. Trav. Chim. Pays-Bas*, 1931, **50**, 936).

D. G. H.

New Stereoisomer of Elaeostearic Acid in Pomegranate Seed Oil. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 182–185B.)—The new acid isolated from pomegranate seed oil (*Punica granatum*. L.), called "punicic" acid, was prepared by recrystallising the magnesium soaps of the mixed fatty acids of the oil. It had:—m.p. 43·5 to 44° C.; sp.gr. 50°/4° C., 0·9027; n_D^{50}, 1·5114; molecular refraction 92·4; iodine value (Wijs, 73 per cent. excess of reagent for 2 hours), 209·0 (calc. 273·7); neutralisation value 200·9. If stored under hydrogen, the acid remains unaltered, but in a stoppered bottle it deposits crystals of β-elaeostearic acid. It yielded a tetrabromide identical with that of elaeostearic acid. The ozonide was obtained and decomposed with water, and the products examined. Among them *n*-valeric and azelaic acids were identified, and the presence of oxalic acid and glyoxal was indicated. Ozonolysis of the methyl ester of punicic acid and subsequent decomposition yielded methyl hydrogen azelate and its semi-aldehyde. The formula of the acid is identical with that of elaeostearic acid. D. G. H.

New Stereoisomer of Elaeostearic Acid from the Seed Oil of Karasu-uri (*Trichosanthes cucumeroides*). **Y. Toyama and T. Tsuchiya.** (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 185–187B.)—One hundred seeds of the karasu-uri, a cucurbitous climbing plant of Japan, weighed 14·8 g. and yielded 15·6 per cent. of a reddish-orange oil (dark green in reflected light), with the following characteristics:—sp.gr. at 15°/4° C., 0·9362; n_D^{15}, 1·500; saponification value, 191·2; iodine value (Wijs), 166·7; acid value, 1·87; and unsaponifiable matter, 1·36 per cent. The oil dries rapidly to an opaque film. The mixed fatty acids contained no linolic acid, and the new trichosanic acid was isolated by a procedure similar to that used for punicic acid (see preceding abstract). It had m.p. 35°–35·5° C.; sp.gr. at 50°/4° C., 0·9023; n_D^{50}, 1·5111; molecular refraction, 92·4; iodine value (Wijs; 70 per cent. excess of reagent for 2 hours), 200·0 (calc. 273·7); neutralisation value 200·1. A crystalline bromide was formed (m.p. 113°–113·5° C.) and found to be identical with the tetrabromo-derivative of elaeostearic acid. The acid underwent isomeric change when a petroleum spirit solution was placed under carbon dioxide in a stoppered bottle overnight, and the change was also brought about by adding a minute quantity of iodine, β-elaeostearic acid crystallising out. D. G. H.

Certain Vegetable Tannins and their Conversion into Anthocyanidins. W. J. Chater. (*J. Int. Soc. Leather Trades' Chem.*, 1935, **19**, 218–220.)—Certain anthocyanidins may be reduced to tannins by hydrogen in the presence of a platinum catalyst (*cf.* Freudenberg and co-workers, *Ann.*, 1925, **444**, 153; 1934, **510**, 193), and the process may be reversed by oxidation with a hot mixture of technical dioxan and bromine (*cf.* Appel and Robinson, *J. Chem. Soc.*, 1935, **91**, 426). The author observed that a full, dark red colour was produced when powdered commercial quebracho extract was warmed with dioxan, a hot mixture of bromine and dioxan then added, and the mixture boiled gently for 30 seconds and then cooled. Subsequent dilution with methyl alcohol produced a dark wine-red liquid which became brighter on addition of 0·5 per cent. of hydrochloric acid, and the mixture then had the indicator properties of a solution of an anthocyanidin bromide. Thus sodium acetate produced the violet colour-base, and addition of sodium hydroxide in increasing quantities changed this, first to the blue sodium salt, and then through green, to the brownish-yellow pseudo-base. The fraction of chestnut extract which was soluble in methyl alcohol gave the same series of colour-changes, except that the final shade was brown with a pink tinge; the insoluble fraction gave no red oxidation product. The natural tannins of divi-divi pods, oak galls, myrobalans, sumach or all valonia gave orange-yellow products which usually became yellow on addition of 0·5 per cent. of hydrochloric acid, and formed white insoluble, or colourless soluble products when this solution was then made alkaline. Gambier gave a deep orange-red oxidation product, and mimosa a dark brown-red colour. Similar results were obtained by the use, as oxidising agents, of bromine in ethyl acetoacetate (*cf.* Robinson, *loc. cit.*) and of dioxan-chlorine. J. G.

Starch and Related Polysaccharides of Certain Hard-woods. I. The Preparation and Properties of Oak and Walnut Starch. W. G. Campbell. (*Biochem. J.*, **1935**, **29**, 1068–1080.)—After a preliminary extraction with water at 60° C., to remove tannins, starch may be extracted from wood-meal by treatment with water at 100° C. The extracts are concentrated *in vacuo* at 25° to 30° C., and the starch is precipitated with acetic acid and alcohol. The precipitate is dissolved in water, and reprecipitated by the same reagents. This is repeated until all the colouring matters are removed. The residue is then extracted with absolute alcohol-dry benzene, followed by absolute alcohol and finally by dry ether. The product is a pale pinkish-buff powder which gives an intense blue colour with iodine. Oak sapwood contains an average amount of 1·38 per cent., and walnut sapwood 0·43 per cent. of starch. The ultimate analyses gave the following values for oak starch: (i) C, 43·95; H, 6·50 per cent. (ii) C, 44·11; H, 6·41; N, 0·12 per cent.; and ash, a trace. The values for walnut starch were (i) C, 44·29; H, 6·41 per cent. (ii) C, 43·96; H, 6·44; N, 0·51; ash, 1·13 per cent. The specific rotation of the water-soluble fraction was $[\alpha]_D^{20} = +164{\cdot}3°$, and in 2 per cent. sodium hydroxide solution this became $[\alpha]_D^{20} = +128{\cdot}8°$. The action of taka-diastase on the wood starch gave a maximum of only 89·5 per cent. conversion. Wood starch appears to be an acid polysaccharide of which 90 per cent. is composed of anhydroglucose residues. The remainder is probably glucose-glucuronic anhydride, which may or may not be partly methylated. It is considered that wood starch is a suitable source of nourishment for the larvae of *Lyctus* powder-post beetles. The cell-walls of oak sapwood contain a polysaccharide which is chemically related to the starch of the cell-contents. S. G. S.

Determination of Urushiol in Lacquer. S. Hirano. (*J. Soc. Chem. Ind. Japan*, **1935**, **38**, 219–220B.)—Miyama's method for the determination of urushiol in lacquer consists in extracting the substance with absolute alcohol and titrating the solution with 0·25 *N* barium hydroxide solution, using phenolphthalein as indicator and assuming 0·1 g. of pure urushiol to require 2·46 ml. of barium hydroxide solution. Results are too low, however, on account of oxidation and polymerisation, and vary with the conditions of titration and quantity of indicator. Error of titration is lessened by using a more concentrated solution of urushiol, but the end-point is then difficult to determine. The most concentrated solution that can easily be titrated contains 0·1 g. of urushiol per 20 ml. of absolute alcohol, but 0·05 g. gives a sharper end-point. The change of colour of the indicator ranges over about 0·5 ml. for 0·1 g. of pure urushiol. Preliminary extraction should be with cold alcohol, and the method is of no value when applied to finished lacquers which have been heated to improve the lustre and smoothness. If other solvents, such as benzene or acetone, are used, the titration value is altered. A modification of the method takes the red colour developed in the titration by urushiol, and regarded by Miyama as due to special colouring matter in the lacquer, as end-point of the titration, ignoring the intermediate colour changes, and in this case 0·1 g. of pure urushiol requires 2·07 ml. of the barium hydroxide solution. The red colour takes some time to develop, and if a quicker and better defined end-point is required, more baryta should be added, the maximum value being obtained when the red colour appears immediately after titration. Hydrourushiol (made by hydrogenation and distillation of urushiol) also develops a red colour, with a maximum value of 2·70 ml. of baryta for 0·1 g. of sample, indicating that the end-reaction is a result of oxidation in alkaline solution. The method is not capable of general application. D. G. H.

Inorganic

Use of Vanadous Sulphate as a Volumetric Reducing Agent. P. C. Banerjee. (*J. Indian Chem. Soc.*, **1935, 12**, 198–203.)—Vanadous sulphate solution was prepared by electrolytic reduction at a lead cathode of vanadyl sulphate in dilute sulphuric acid. It was standardised by titration with ferric alum in acid solution, thiocyanate being used as indicator; reduction of the ferric salt was complete at the ordinary temperature. Test experiments showed that vanadous sulphate may be used to titrate ferric iron, copper and chromate in a similar manner to the well-known titanous chloride titrations. S. G. C.

Colour Reaction of Manganese with Formaldoxime. E. Kahane. (*Ann. Chim. anal.*, 1935, **17**, 175–178.)—*Reagent.*—Two g. of hydroxylamine hydrochloride are dissolved in 50 ml. of water and 1 ml. of 40 per cent. formaldehyde is added, yielding a solution of formaldoxime. *Method.*—A few ml. of the solution to be tested are made alkaline with sodium hydroxide, sodium carbonate or ammonia, and one or two drops of reagent are added. Manganese gives a stable purple colour which reaches maximum intensity within a few minutes, and is independent of the initial stage of oxidation of the manganese. The smallest amount of manganese detectable in a 10-cm. column of liquid is 0·02 mg. per l. The colour may be compared colorimetrically with a standard. Various other metals yield colours under similar conditions. Iron gives a brownish-violet colour perceptible with 1 mg. per l., but iron may be removed prior to the test for manganese by shaking the solution for a minute or two with a suspension of zinc oxide and filtering. Copper produces a violet colour when present in small amount (sensitiveness 0·5 mg. per l.) or a green colour in stronger solution. Nickel gives a green to brown colour (0·5 mg. per l. detectable), whilst with cobalt a yellow colour is obtained when more than 20 mg. per l. are present. S. G. C.

Volumetric Determination of Manganese. J. Leroide and A. Bruiltet. (*Bull. Soc. Chim.*, 1935, **2**, 740–742.)—The Volhard titration of manganese with permanganate has been tried in a modified form, the zinc acetate or sodium acetate, usually added, being replaced by a considerable amount of alkali sulphate. To the neutral manganese solution (500 ml.) were added 50 g. of potassium sulphate or 90 g. of sodium sulphate decahydrate. The boiling solution was titrated with

N/10 permanganate solution until a faint rose colour persisted for 4 minutes. Practically the theoretical result was obtained, the calculation being based on the equation: $3Mn^{II} + 2Mn^{VII} = 5Mn^{IV}$. In the presence of 0·5 g. of ferric sulphate or 10 g. of sodium chloride the results were low by 0·8 per cent. S. G. C.

Quantitative Separation of Nickel and Cobalt by Means of Triethanolamine. E. Raymond. (*Compt. rend.*, 1935, **200**, 1850–1852.)—In the following method the quantities of reagents given are appropriate for 1 gram-atom proportion of metal. To the solution containing nickel and cobalt are added an excess (10 mol.) of a 20 per cent. solution of triethanolamine [$N(CH_2CH_2OH)_3$] and an excess of sodium hydroxide (100 mol.). The liquid is diluted to 100 l. and heated to boiling. The nickel precipitates as hydroxide, leaving the cobalt in solution as a violet-coloured ammine. The nickel hydroxide is filtered off, washed with *N*/100 sodium hydroxide solution, dissolved in dilute sulphuric acid and determined, by *e.g.* electrodeposition, in the usual way. The filtrate is neutralised with sulphuric acid, an excess of urea (150 mol.) is added, and the cobalt is deposited by electrolysis, the details of which are similar to those of the normal process. Iron behaves in a similar manner to cobalt in the process, and must therefore be previously removed. Accurate results were obtained with 0·003 to 0·25 g. of nickel and cobalt present in various proportions. S. G. C.

Determination of Chromium in Stainless Steel. G. F. Smith and G. P. Smith. (*J. Soc. Chem. Ind.*, 1935, **54**, 185T–189T.)—To a 0·5-g. sample of the finely-divided steel, contained in a 500-ml. conical flask, are added 10 ml. of a mixture of 1 vol. of 70 to 72 per cent. perchloric acid and 2 vols. of 85 per cent. phosphoric acid. The mouth of the flask is closed by a thistle-funnel having the stem about 4 inches long, sealed off, and bent to bring the end into contact with the inside surface of the flask; the funnel should have a small indentation to prevent a vapour-seal. The flask and contents are heated at 175 to 185° C. on a hot-plate for 3 to 5 minutes, when the steel dissolves to a green solution, the chromic salt remaining unoxidised. Then 15 ml. of a mixture of 1 vol. of 70 to 72 per cent. perchloric acid and 2 vols. of 80 per cent. sulphuric acid are added, and the temperature is raised to 203 to 205° C. After 4 to 5 minutes the chromic acid colour appears, and the oxidation is complete in a further 3 minutes, the solution attaining an orange colour. At this point 10 to 20 mg. of potassium permanganate crystals are added, the flask is immediately removed from the source of heat, and, with a swirling motion, is dipped into ice-cold water for 6 to 7 seconds. (As a precaution against breakage, the flask should be first dipped momentarily and then returned to the cooling-bath. The addition of permanganate, followed by rapid cooling, was found necessary in order to overcome a slight tendency to low results, due to a side-reaction of chromic acid with perchloric acid at the high temperature.) The solution is immediately diluted to 60 to 70 ml. with cold water; 0·5 ml. of conc. hydrochloric acid is added, and the solution is boiled for 5 minutes to remove chlorine, and then cooled by diluting to 250 ml. with ice-water. For the titration, 2 drops of 0·025 *M* *o*-phenanthroline ferrous ion indicator solution are added, followed by a measured excess of 2 to 3 ml. of 0·1 *N* ferrous sulphate solution, producing a pinkish colour. The excess of ferrous sulphate is back-titrated with 0·01 *N* ceric sulphate solution, the end-point being marked by a transition from pink to green. Results in good agreement with, but very slightly higher than, the certificate values, were obtained in trial determinations of chromium in Bureau of Standards standard steels. S. G. C.

Identification of the Alkaline Earths in Admixture. N. A. Tananaeff. (*Z. anal. Chem.*, 1935, **100**, 391–394.)—Glacial acetic acid can be used like alcohol as a selective solvent for the alkaline earths; it dissolves the nitrates of calcium and magnesium, but not those of barium and strontium. The chlorides of calcium and magnesium are soluble in the glacial acid; barium chloride is insoluble. The test is carried out by evaporating the solution to dryness, stirring and warming the residue with 10 drops of acetic acid. The extract is tested for calcium and magnesium, the residue for barium and strontium (chromate method). Strontium may be detected more expeditiously by the flame test, which can be carried out by heating the residue from the acetic acid extraction on a platinum lid inclined towards the Bunsen flame. During the decrepitation of the salt, minute particles are projected into the flame and produce the characteristic colour. Calcium may be identified in presence of barium and strontium, but not of magnesium, by means of potassium ferrocyanide*. One drop of the saturated salt solution is evaporated to dryness with 10 drops of saturated ferrocyanide solution; the residue is stirred with 40 drops of water, calcium producing an opalescence. The method is particularly adapted for the detection of calcium in strontium salts. In this case 10 drops of water are added, one by one, while the residue is being stirred; it remains insoluble, but the cloudiness or opalescence of the solution reveals the presence of calcium. In a mixture of the four alkaline earth metals, magnesium is first separated by precipitation of the three other bases with ammonium carbonate. Calcium is then identified by the ferrocyanide reaction. If present, it is extracted from the dry nitrate residue in a separate portion by glacial acetic acid; the insoluble residue is then tested for strontium by the flame reaction and for barium by means of potassium chromate. W. R. S.

*With regard to the ferrocyanide test for calcium no mention is made of conditions of acidity, etc., but it would seem obvious that both free acid and ammonium salts must be absent, as these themselves cause precipitation when heated with ferrocyanide.—EDITOR.

Microchemical

Microchemical Reactions of Pyramidone. M. Wagenaar. (*Pharm. Weekblad*, 1935, **72**, 612–615.)—The sensitiveness and minimum concentration detectable are given in brackets after each reaction. The solubility of pyramidone in water is 1 : 17, but considerably less in the presence of sodium chloride, and addition of a crystal of the latter to a drop of a solution in water produces a precipitate of block-shaped crystals (0·1 mg.); this method is preferable to sublimation as a means of identification by separation. Mayer's reagent (0·05 mg., 1 : 200) or solutions of potassium cadmium iodide or of potassium zinc iodide (0·2 mg., 1 : 100) give similar block-shaped (or sometimes triangular) yellow-white crystals having angles of 60° and 120°; it is an advantage to add a drop of acetone, which should subsequently be removed by evaporation. The reaction is unaffected by the presence of hydrochloric, sulphuric or acetic acid, and in the case of potassium zinc iodide it is assisted by the presence of hydrochloric acid (*cf.* Weehuizen, *id.*, 1906, **43**, 1105). Substitution of the potassium iodide in Mayer's reagent by potassium thiocyanate gives isomorphous crystals which are very stable; the m.p. of these might be used as a means of identification, and further work on such lines is in progress (*cf.* Kolthoff and Hamer, ANALYST, 1925, **50**, 90). Platinum chloride in acid solution produces crystals which have the violet colour of the oxidation-product of pyramidone (*cf.* following abstract); precipitation is accelerated by scratching (0·1 mg., 1 : 100). Gold chloride in the presence of nitric acid gives small yellow needles which form star-shaped groups (0·05 mg.; 1 : 200); a black colour is produced immediately if an acid without oxidising properties is substituted for nitric acid. Picric acid produces block-shaped crystals on scratching (0·1 mg., 1 : 200). *p*-Nitrophenol forms groups of needles (0·1 mg., 1 : 200), but the corresponding *o*- and *m*-compounds, and dinitrophenol, are all unsatisfactory for this purpose. A solution of iodine in potassium iodide solution containing hydrochloric, acetic or sulphuric acid gives a heavy precipitate, which, on scratching and addition of a drop of acetone, forms dichroic block-shaped crystals; these are yellow and have a woolly appearance or else are block-shaped (0·02 mg., 1 : 200). An acidified solution of bromine in potassium bromide solution produces green needles; the reacting drops should be shielded from the light, and the sensitiveness is low (1 : 100). Quinosol forms groups of star-shaped crystals (0·2 mg., 1 : 100), and may therefore be used in the presence of antipyrine, which does not react (*cf.* abstract, p. 560). J. G.

Microchemistry of Antipyrine. M. Wagenaar. (*Pharm. Weekblad*, 1935, **72**, 642–644.)—The sensitiveness and maximum dilution of the reactions are given in brackets. When antipyrine is sublimed on to a cooled surface it forms thin crystals similar to "ice flowers" (*cf.* C. Van Zijp, *id.*, 1933, **70**, 1245), and these may be used for the tests described, or even as a means of identification (1 mg.). The solubility of antipyrine in water is greatly decreased if sodium chloride is present, and numerous *d*-rotatory block-shaped crystals are produced on scratching, after addition of a crystal of common salt to a drop of a solution of antipyrine in water. Interference colours can be seen, and the two types of crystals described by Van Zijp (*loc. cit.*) are recognisable, *viz.* hexagonal plates with angles of 128° and 116°, and oblong crystals with an angle of 66°. If antipyrine is warmed with nitric acid, a violet colour results, and, on complete removal of the acid by evaporation, groups of white needles are produced which may conveniently be recognised by the use of crossed Nicols (2 mg.). The nitrous acid reaction is the best available, and block-shaped sea-green crystals are produced if a drop each of sodium nitrite solution and hydrochloric acid is added to the crystals obtained by salting-out antipyrine from a solution in water, as described above (0·1 mg., 1 : 300). Potassium ferrocyanide (after Behrens), followed by sulphuric acid produces thin lozenge-shaped crystals (having an angle of 82°) in star-shaped aggregates (0·1 mg., 1 : 200). Star-shaped groups of needles are produced on adding a drop of acetone and then a crystal of potassium ferricyanide to a solution of antipyrine in a drop of dilute hydrochloric acid (0·2 mg., 1 : 200). No precipitate results if a crystal of sodium nitroprusside is placed in a drop of a solution of antipyrine in water, but if hydrochloric or sulphuric acid is then added, bundles of crystals are deposited on scratching (0·1 mg., 1 : 200). Platinum salts in the presence of hydrochloric acid (after Behrens) form, on scratching, light yellow crystals having an angle of 140° (0·2 mg., 1 : 200). If a crystal of sodium iodide is then added, black crystalline masses result which form dark red feather-shaped crystals; this reaction is less sensitive, but more characteristic than that obtained with the simple platinum reagent.

J. G.

The Micro Copper-Pyridine Reaction of Certain Organic Acids. A. J. Steenhauer. (*Pharm. Weekblad*, 1935, **72**, 667–669.)—Zwikker's reaction for barbituric acid and its derivatives (ANALYST, 1931, **56**, 758) is applied to other organic acids, a crystal of the sample being added to a drop of a mixture of 4 ml. of a 10 per cent. copper sulphate solution, 1 ml. of pyridine and 5 ml. of water; the crystal-growths are observed under the microscope. The best results are obtained with salicylic and acetylsalicylic acids. The former produces green-blue prisms or irregular hexagons, although if the sodium salt is used, the precipitate is first amorphous and then crystallises. The latter (or its calcium salt) deposits purple-blue prisms, squares and hexagons on scratching, and these are usually *d*-rotatory, and, like the salicylic acid compound, are double-refracting. Benzoic acid and its salts give double-refracting, dichroic, colourless or blue prisms in star-shaped groups. A solution of cinnamic acid in ammonia precipitates rosettes of fine double-refracting prisms, which subsequently develop a leafy structure; the colour, which is blue-green, is best seen by incident light. Anisic acid forms star-shaped groups consisting mainly of colourless to blue, double-refracting dichroic, *d*-rotatory sloping prisms. With anthranilic acid, green, double-refracting hexagonal plates and lens-shaped crystals are produced, and fumaric acid slowly precipitates blue crystalline masses. These crystal-forms are all illustrated.

J. G.

Physical Methods, Apparatus, etc.

Irradiation of Fats. I. A Standardised Method of Use of Ultra-Violet Light. L. H. Lampitt, N. D. Sylvester and P. Bilham. (*Biochem. J.*, 1935, 1167–1174.)—By means of the apparatus described, which gives reproducible results, fats may be irradiated by ultra-violet light, the intensity of which is measured by a photo-electric cell. The vessel containing the fat is maintained at a constant temperature in a thermostat, and the fat itself is stirred by mechanical means. It has been found that, for butter fat, the peroxide value, the Issoglio value and the colour in the Kreis test, all increase with increasing light intensity and with increasing time, and that a change of temperature of the fat changes any relationship which may have existed between these three values. S. G. S.

Review

THE SPIRIT OF CHEMISTRY. By Professor A. FINDLAY. Second Edition. Pp. xvi + 510, with 152 illustrations. London: Longmans, Green & Co. 1934. Price 10s. 6d. net.

The scope of this work has previously been described in a review of the first edition (ANALYST, 1931, **56**, 140), and in the present volume a few additions have been interpolated on coal-tar dyes, and synthetic drugs and perfumes. In the production of this comprehensive manual, the author has carried out a difficult task with conspicuous success, the presentation being such that even the more abstruse branches of the subject will present no insuperable difficulty to the reader with little knowledge of science.

The first glance through this book gives the impression that an inordinate proportion of the text has been devoted to inorganic and physical chemistry, but further investigation dispels this idea, since organic chemistry is advantageously woven in with the rest, in addition to the four final chapters dealing with it. In reviewing the second or subsequent editions of any text-book more rigid criticism is, perhaps, called for than when one is dealing with a new production, and although no serious errors have been encountered in this volume, there are a few of minor importance which require modification.

Whilst "hydrogen ion concentration" is described, the more widely-known expression "*p*H value" appears to be entirely omitted, although many readers would naturally turn to the volume for a definition and explanation of the latter. Numerous references are made in the text to other portions of the book; in some instances the number of the page referred to is given, but too frequently this is omitted, with consequent annoyance and loss of time of the reader. In this connection it may be noted that two references on pp. 188 and 241 are wrongly numbered. *Mycoderma aceti* is quoted on p. 451 as an example of a mould or bacterium, although it is not a member of either of these classes. The numerous illustrations, whether diagrammatic or photographic, are on the whole excellent, but those on pp. 194, 196 and 305 suffer from loss of detail in the lighter tones.

Notwithstanding these minor faults, the volume is of great educational value and contains much matter of interest not only to the readers for whom it primarily is intended, but to a far wider circle. In addition, the humanistic touch contributed by the numerous brief biographies of famous scientists adds a living interest to what many students have found to be a mere list of names associated with scientific laws, apparatus, and so on.

The volume reflects great credit upon the author, for it would be difficult to find one better adapted to stimulate the interest of the reader in the principles of chemistry and applied science and to induce the perusal of more advanced works, such as those cited in an appendix at the end of the book.

T. J. WARD

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SEPTEMBER, 1935 Vol. 60, No. 714

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Deaths

WITH great regret we record the following deaths:

Mr. S. F. Burford on August 29th.
Mr. C. T. Kingzett on July 29th.
Mr. A. C. Wilson on July 15th.

Obituary

LEONARD ARCHBUTT

OUR Society mourns the loss of Leonard Archbutt, who died at Bournemouth in April last in his 78th year. He leaves a widow, three sons and eight grandchildren, to all of whom the sympathy of the Society is extended. He was educated at private schools and afterwards at University College School, London, where the late Charles E. Cassal was a fellow pupil.

He worked in the laboratory of the late Alfred H. Allen for several years, first as an articled pupil and then as an assistant, and in January, 1881, was appointed chief chemist to the Midland Railway Company, with headquarters at Derby. Upon the amalgamation of the various companies, Archbutt was chosen for the important post of chief chemist to the London, Midland & Scottish Railway Company, and this he held until his retirement in 1923. The remainder of his days were spent at Burnham-on-Sea, Somerset, and latterly at Bournemouth.

He was elected a Fellow of the Institute of Chemistry in 1888, and served on the Council and its Committees for a number of years during the period 1897 to 1926.

One of his most marked characteristics was his great orderliness and precision of mind, notable in his professional work and in everyday affairs. His laboratory, his office and his private den reflected this; indeed, with him everything must be, and indeed was, "just-so." The writer often marvelled at the skill and energy with which he attacked the manifold complex problems occurring in his work, and his enthusiastic and persistent pursuit of their solution. The scope of his work was of enormous extent, covering general analytical, commercial, metallurgical and engineering chemistry. His knowledge was truly encyclopaedic. Perhaps his greatest love was for the chemistry of oils and fats.

In 1893 he was appointed a member of the Standing Committee of Railway Goods Managers, afterwards the Dangerous Goods Committee, and in 1894 of the Committee of Railway Chemists, both meeting at the Clearing House, and he retained his membership until his retirement. He was Chairman of the latter Committee for sixteen of the twenty-nine years of his service. During the war he was appointed by H.M. Government to a Standing Committee concerned with the carriage of explosives.

Archbutt joined this Society in 1894, and, after serving on the Council for several periods, and then as a Vice-President for two years, was elected President for the years 1912 and 1913. His election constituted a notable advance in procedure, as he was not a Public Analyst or intimately concerned with food analysis; he became, therefore, the first representative of the "Other Analytical Chemists" included in our title in 1906. The writer knew his very high appreciation of the honour, although, with the modesty characteristic of him, he at first expressed surprise at his nomination. He filled the office with distinction and with the applause of his colleagues. From 1884 to 1913 he made many contributions to THE ANALYST, mainly connected with the examination of oils and fats and with metallurgical problems. The writer well remembers two outstanding papers on the "Determination of Oxygen in Copper" in 1900 and 1901, and his demonstration of the process at Burlington House.

He was also responsible for the Section on "Special Characters and Methods" in Vol. II of the Fourth Edition of *Allen's Commercial Analysis*, 1910. This volume was concerned with "Fixed Oils, Fats and Waxes."

As an author, Archbutt will always be best remembered by his book, *Lubrication and Lubricants*, written in collaboration with R. M. Deeley; it was first published in 1899, and reached its fifth edition in 1927. The writer may be allowed to quote the concluding sentence of the review by Dr. J. T. Dunn on this book (ANALYST, 1927, **52**, 562): "Nothing but praise can be given to the work, and the authors are to be congratulated on having maintained the high standard of achievement which they had already reached." In a recent letter to the writer, Archbutt expressed the pleasure he derived from undertaking his share of the new edition during his retirement.

As a result of earlier collaboration between Archbutt and Deeley, an apparatus was devised and patented by them, about 1890, known as the "Archbutt–Deeley Water Softening Plant"; this was manufactured and marketed by Messrs. Mather & Platt, Manchester, and had very considerable success. Briefly, the water was treated in batteries of rectangular tanks with the appropriate reagents and mixed; compressed air was then blown upwards through the water from perforated pipes at the bottom. On cutting the air off, subsidence of the precipitate was so rapid that the clear softened water could be drawn off through floating arms in a remarkably short time.

Archbutt was a staunch adherent of the Society of Chemical Industry, and was in early days one of the mainstays of the Nottingham Section, supporting it by his regular attendance and by many contributions, both to the Section and to the Society.

He had not much leisure for public affairs, but in 1919 was elected by the Town Council of Derby a co-opted Member of the Education Committee, and by them appointed to the Higher Education Committee, resigning on leaving Derby. In far earlier days he was a part-time teacher under the Technical Instruction Committee.

And what of Archbutt the man, as the writer knew him? A genial host, a welcome guest, a pleasant companion, and, withal, of cultured mind and wide reading. He was fond of music, and at one period devoted much time to the cult of the violin. The writer owes to him his introduction to the game of golf; together long rambles round the countryside were constantly made, and more lengthy and adventurous cycle rides were undertaken. Later he became a fairly ardent motorist, and in recent years, as the above forms of exercise became too strenuous, relied mainly upon his car for his recreation.

On the lighter side, and in less responsible days, he joined in our impromptu "Smokers" at the Golf Club, with their rollicking choruses, and, if memory serves, his favourite song for his own turn was "The Vicar of Bray."

And so the writer bids farewell to Leonard Archbutt, holding him in memory not only as a man of learning and great ability, but also as a companion and a friend.

JOHN WHITE

The Examination of Therapeutic Oxygen

BY ROBERT C. FREDERICK, F.I.C.

THE methods to be employed in the examination of oxygen to determine its purity for medical purposes have assumed additional interest and importance now that this gas has been included, for the first time, in the British Pharmacopoeia.[1] The monograph inserted follows that in the earlier United States of America Pharmacopoeia[2] very closely, and the only difference in matters of fact is that whilst the former gives the solubility of oxygen as about 1 in 43 volumes of water the latter records this as being 1 in 34.

CARBON DIOXIDE, HALOGENS, ACIDS, ALKALIS, OXIDISING SUBSTANCES.—The tests for purity specified in these Pharmacopoeias are directed to determine whether the sample complies with certain limits for carbon dioxide, halogens, acids, alkalis, and oxidising substances, and finally, the "assay" of the oxygen-content. These tests, except the assay, all require the sample to be passed through reagents at stated rates of flow. The fitting of a fine adjustment reducing-valve to the cylinder is therefore essential, and it may be noted that such valves are obtainable with a supplementary gauge showing the rate of flow in litres per minute, the notation used in the tests referred to above.*

CARBON MONOXIDE.—In addition to these tests I examine for carbon monoxide, employing for this purpose, on account of its convenience, sensitivity, and rapidity in action, a proprietary material, "Hoolamite," devised by Lamb and Hoover (U.S. Pat. 321,061 and 1,321,062). Hoolamite[3] is a mixture of pumice stone, iodine pentoxide and fuming sulphuric acid which, on reaction with carbon monoxide, changes in colour from dirty white to blue-green and violet-brown, and the depth of colour produced is proportional, but not exactly so, to the amount of carbon monoxide. The test can be made roughly quantitative by reference to permanent colour standards. A number of other substances give the same reaction, particulars of which will be found in the literature cited,[3,4] but all these are absorbed by prior passage through dry active charcoal. The material is put up by the manufacturers† in glass tubes, about 11 cm. long and 5 mm. external diameter; the ends are drawn out, sealed, and covered for a distance of about 3 cm. from each end with a scarlet paint, leaving a length of about 5 cm. available for observation of the result of a test. In use, the tubes are easily opened by breaking off the ends after making a stroke with a file. The colour produced with carbon monoxide disappears in a short time and, if the ends have been kept sealed with rubber tubes carrying a piece of glass rod when not in use, the tubes can be employed for six tests or more, provided that the carbon monoxide concentrations encountered have not exceeded 0·2 per cent.

In examining oxygen I use a glass tube, about 42 cm. long and 8 mm. in diameter, packed with active charcoal (obtainable with the Hoolamite tubes) held in position by plugs of glass wool. One end is connected to the oxygen discharge and the other to a Hoolamite tube in train. The oxygen is passed through at the arbitrarily chosen rate of 500 ml. per minute for four minutes, and observation of the appearance of the tube is made immediately after. As a precautionary measure the train is wrapped in a towel during the passage of the gas. Hoover claims that, under favourable conditions, 0·005 per cent. of carbon monoxide can be detected. Katz and Bloomfield,[4] in their tests of a small portable carbon monoxide detector employing Hoolamite with 350 to 700 ml. of air, found that with this apparatus 0·06 per cent. and less gave no noticeable colour-change, and in a few instances there was no indication with 0·07 or even 0·08 per cent., but there was no failure to indicate carbon monoxide when the concentration was higher than the last figure.

THE DETERMINATION OF THE OXYGEN-CONTENT.—A discussion of the method to be employed in determining the oxygen-content is, however, the primary purpose of this communication.

Pharmacopoeia Method.—The method which the British Pharmacopoeia requires is given there in such brief outline that it may be quoted in full: "Shake in a calibrated tube about 50 millilitres, accurately measured, with 10 millilitres of alkaline solution of pyrogallol; not less than 98 per cent. v/v is absorbed." In Appendix I (p. 507) the directions for preparing the pyrogallol solution are that 0·5 g. of pyrogallol is to be dissolved in 2 ml. of water and 12 g. of potassium hydroxide in 8 ml. of water; the two solutions are to be mixed immediately before use.

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* That used by the author is the "Pinson" valve, manufactured by The Manchester Machine and Instrument Manufacturing Co., Ltd., 202-204, Sheald Grove, Rusholme, Manchester.

† Mine Safety Appliances Co., Pittsburgh, Pa., U.S.A. (obtainable from Messrs. Siebe, Gorman & Co., Ltd., 187, Westminster Bridge Road, London, S.E.1).

Alkaline pyrogallol has been used for the determination of oxygen in gaseous mixtures since 1851, at least, and is probably still the reagent most commonly employed, though it has been known since 1863 that carbon monoxide may be produced in the reaction; each part of carbon monoxide formed causes an underestimation error of 0·5 part of oxygen. There is an extensive literature dealing with the circumstances under which this occurs and with its prevention. One factor which it is desirable to emphasise here is the influence of the amount of oxygen present in the gaseous mixture being treated; solutions of alkaline pyrogallol which yield no significant quantity of carbon monoxide when used with gaseous mixtures in which the oxygen-content is of the order of that present in air, fail to maintain this inhibitory quality when employed with gaseous mixtures in which the amount of oxygen is of the order of that found in commercial samples of the gas. A multiplicity of formulae for the preparation of alkaline pyrogallol have been recommended, and Drakeley and Nicol,[5,6] in their exhaustive researches on the use of this reagent in the examination of cylinder oxygen, found that every one they investigated evolved carbon monoxide when such oxygen was absorbed, and that, even in analysis for ordinary industrial purposes, the oxygen should be diluted to about 25 per cent. with nitrogen. Lunge and Ambler[7] categorically state that in the examination of oxygen for purity pyrogallol should not be used.

Drakeley and Nicol (*loc. cit.*) found the most satisfactory solutions to be those due to Anderson[8] and Haldane[9]; both of these solutions are prepared with a solution of potassium hydroxide, sp.gr. 1·55 (*i.e.* about 80 g. KOH per 100 ml.); in the former 15 g., and in the latter 10 g., of pyrogallic acid are dissolved in each 100 ml. The proportions in the solution specified in the Pharmacopoeia, with the exception that the pyrogallic acid is dissolved in 2 ml. of water instead of 1·5 ml., are those recommended by Hempel[10] over 40 years ago. In all three solutions the amount of potassium hydroxide is approximately the same, but in that given by the Pharmacopoeia the amount of pyrogallic acid is only about one-third of that in Haldane's, and about one-fourth that in Anderson's. The point is of importance, in view of the finding, by Drakeley and Nicol, that a considerable excess of potassium hydroxide and a high concentration of pyrogallol tend to diminish the production of carbon monoxide. The Haldane solution referred to above is that recommended by the originator of the well-known general air-analysis apparatus of that name for use therein. Haldane and Makgill,[11] in a comparatively recent communication, give an account of experiments which were carried out with this apparatus, showing that whilst a small quantity of carbon monoxide was produced when the solution was used immediately after preparation, none was produced if the solution was allowed to stand for 70 hours at room temperature or was heated in a water-bath for one hour before use. In considering the bearing of this observation on the use of alkaline pyrogallol in the examination of cylinder oxygen, it has to be remembered that in any determinations made by the Haldane

General Air Analysis Apparatus the oxygen cannot have been present in the apparatus in excess of 30 per cent., for the fine graduations do not extend beyond this; when a larger percentage of gas is present, the sample requires to be diluted. Professor J. S. Haldane, in a personal communication, has kindly informed me that ordinary air was used in their experiments. I have not made any extended investigations, but in a number of samples I have tested the residual gases remaining after the absorption of cylinder oxygen by a strong solution of alkaline pyrogallol (10 g. of pyrogallic acid in 125 ml. of nearly saturated potassium hydroxide solution) which had been stored, sealed, and unused, for six months or more, and in most of these cases the presence of carbon monoxide was quite evident.

Apart from the choice of absorbent, the technique of the assay outlined in the Pharmacopoeia is open to criticism. The absorption of about 49 ml. of oxygen with only 10 ml. of reagent entails the production of a pronounced negative pressure in the apparatus. Absolute tightness of stopcocks is difficult to maintain, and a slight imperfection which, in the more usual procedure of having an excess of reagent arranged to occupy immediately the space formerly occupied by the gas, would be unimportant, may in these circumstances introduce an appreciable error. The use of 50 ml. of the sample, instead of 100 ml., will double any experimental error, and it is difficult to understand circumstances arising in which this conservation of the sample is necessary, for, unless there is an adequate quantity available for the preliminary flushing out of connecting tubes from the sample container, an accurate determination is impossible.

The Copper-Ammonia Method.—An absorbent which is free from the disadvantages of alkaline pyrogallol when used in the examination of cylinder oxygen is metallic copper in contact with ammonia, as devised by Hempel.[12] Indeed, it is only for oxygen of high purity that this medium can be employed directly, for, unless some 90 per cent. of the gas mixture is absorbed, the ammonia tension of the residual gas introduces complications. An apparatus which is supplied* for the frequent tests required in the operative control of oxygen-producing plants embodies the use of this absorbent, and consists essentially of a burette of special design mounted with a Hempel phosphorus pipette.

The apparatus designed by me is based on that referred to above, and is illustrated in Fig. 1. A feature of the stand (not shown) is that the upright is secured to the front edge of the base; although, in consequence, all the actual apparatus is at one edge, stability is assured by having a heavy weight fixed to the underside of the base between the feet. The upright can, therefore, be placed in line with the edge of a bench, and, as it is cut away about the lower graduations of the burette, the levelling-tube can be brought into contact, so that an accurate reading can be made of the volume of sample taken for examination. The upright is also cut away behind the upper graduated portion of the burette, so that the apparatus can be used with the light either on or behind it. There is some tendency for a bubble of gas to collect in the capillary tube near the top of the absorption pipette, and the upright is cut away there, too, so that such an occurrence can be readily detected. The position of the upright also permits of easy access to the bung of the absorption pipette; the bung is secured by a chain

* By the British Oxygen Co., Ltd., Wembley, Middlesex.

held in position by two links slipped over a metal strip clamped to the neck of the absorption pipette. The shape of the stand as a whole facilitates the shaking carried out to promote absorption.

The burette has a capacity of 100 ml. between the stopcock and the final graduation in the lower stem. From the stopcock 5 ml. are graduated downwards in tenths, and from the 100 ml. mark upwards to 99 ml. also in tenths. As these extremities have a narrow bore, it is possible to read to 0·01 ml., if desired. The burette is connected by capillary tubing with the absorption pipette, which, again, is connected by ordinary tubing with a displacement bulb; the upper surface of the absorption pipette is flat instead of round, so that a small quantity of unabsorbed gas is more easily kept in contact with the copper. To the burette a levelling-tube is attached, as shown.

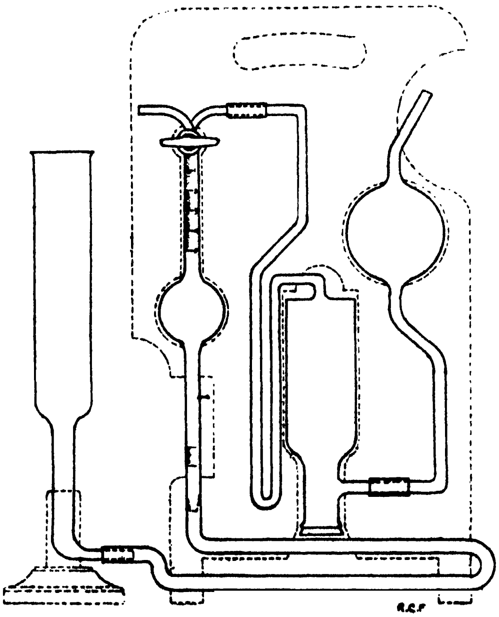

Fig. 1. (Scale, approximately 1 to 6.)

To prepare the apparatus for use, copper wire, W.G.18 or 20, is cut into short lengths and made into "springs" of external diameter less than the bung-hole of the absorption pipette. With the apparatus inverted, the absorption pipette is filled with the copper springs, the last in such a position that it will rest flat on the bung when this is inserted. The ammoniacal solution recommended by Hempel is a saturated solution of ammonium carbonate mixed with an equal volume of ammonia, sp.gr. 0·93. Haehnel and Mugdan[18] advised the use of ammonium chloride instead of carbonate; I have found that this tends to increase the rate of absorption. A solution which has been suggested for use in apparatus of this nature, and which has been found satisfactory in practice, is prepared by mixing 450 ml. of ammonia, sp.gr. 0·880, with 750 ml. of water, and dissolving in this 330 g. of ammonium chloride. With the apparatus still inverted, and the stopcock shut off in all directions, the ammoniacal solution is poured into the absorption pipette nearly to the arm connecting with the displacement bulb; the bung is replaced and secured. With the apparatus restored to its upright position, sufficient of the ammoniacal solution is added to the levelling-tube, so that with suitable manipulation of this and the stopcock, the solution is finally at a height of about 14 cm. in the levelling-tube, with the tube connecting with the burette, the capillary tube, the absorption pipette, the burette, the tube connecting with the displacement bulb all full, and the displacement bulb filled to a height of about 3 cm. The stopcock, having been shut in all directions, is now opened to the short left-hand capillary tube above it and, by raising the levelling-tube, this is also filled with the ammoniacal solution. With the stopcock shut in all directions the apparatus is now ready for use, though with the first few samples the absorption will be rather sluggish.

In taking the sample from a cylinder the fitting of a reducing valve is necessary, and preferably this should be of the type described above, with a length of rubber tubing attached. The oxygen is allowed to discharge for some minutes at a flowmeter reading of 2 to 3 litres per minute to ensure complete removal of air from the cylinder attachments, and is then slowed down to a rate of about half-a-litre per minute. With the oxygen discharge continuing, the rubber tube is brought to the apparatus and connected, with simultaneous cessation of the discharge.

The stopcock is now turned to establish connection with the rubber tubing, and the oxygen is turned on and allowed to discharge very slowly into the burette. This discharge is continued until, with the liquid in the levelling-tube held at the same level as that in the burette, the burette reading is somewhere between 100 and 99·8 ml. The stopcock is shut in all directions and, after allowing time for drainage, the exact reading is made of the quantity of sample taken for examination with, of course, the liquid in the levelling-tube and the burette again at the same level. An alternative to the procedure just described is to take in a quantity of sample in excess of 100 ml. and then to shut off the stopcock in all directions, and disconnect the rubber tube to the cylinder; after allowing time for drainage, the liquid in the levelling-tube is made to coincide with the 100-ml. mark of the burette, and by gradually opening the stopcock the liquid in the burette is allowed to rise to this, and, with the stopcock now shut in all directions exactly 100 ml. of sample have been measured.

In either case the measured quantity of sample is passed over into the absorption pipette by opening the stopcock to establish communication in that direction, raising the levelling-tube, and maintaining it in that position until there is an unbroken column of liquid to the pipette; the stopcock is shut in all directions. In the absorption of the oxygen the copper is tarnished and the oxide formed is removed by gentle shaking of the apparatus, causing the ammoniacal solution to wash over the copper and thus cause the presentation of a fresh bright surface. When absorption is apparently complete the apparatus is left for a few minutes, tilted slightly if necessary, with the residual gas in contact with copper. Thereafter the entire volume of unabsorbed gas is returned to the burette by opening the stopcock in that direction, and lowering the levelling-tube until the capillary tube to the absorption pipette presents an unbroken column of liquid. The stopcock is shut in all directions. A provisional reading of the total volume of gases not absorbed is made after a brief interval to permit drainage to be complete. A repeat absorption treatment is then carried out, and afterwards a check reading of the volume.

If exactly 100 ml. of the sample were taken for the analysis, the volume of residual gas is, of course, in terms of percentage directly; if less than 100 ml. were used, this result is obtained by simple proportion. In either case deduction of this percentage from 100 gives the percentage of oxygen. For the routine examination of commercial oxygen the determination may be expedited without introducing serious error by considering the initial reading of the volume of sample as 100 ml., so long as this is between 100 and 99 ml.; for example, in an extreme case, 100 ml. of a sample giving an unabsorbed volume of 1·55 ml. would give a reading of 1·53 ml. unabsorbed if only 99 ml. had been used for the determination, and the oxygen percentages then would be 98·45 and 98·47, respectively—a difference of 0·02 per cent.

A mixture of oxygen and carbon dioxide, in which the latter gas is usually present to the extent of about 7 per cent., is being employed to an increasing extent for certain therapeutic purposes, and, in considering the analysis of such a mixture, it has to be remembered that, as with alkaline pyrogallol, both gases are absorbed by the copper-ammonia reagent.

SUMMARY.—The methods to be employed in the examination of oxygen for therapeutic use have assumed additional interest now that this gas is included in the British Pharmacopoeia. Some reference is made to the qualitative tests specified therein, and the method for carrying out an additional qualitative test which the author makes (that for carbon monoxide) is described. But it is with the "assay" of the oxygen-content that the paper is chiefly concerned; the method given in the Pharmacopoeia is criticised, and the one used by the author, embodying the copper-ammonia reaction in an apparatus devised by him, is described in detail.

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Determination of Methyl Alcohol in the Air

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It has been recognised for a long time that methyl alcohol is toxic under certain conditions. McFarlane[1] was one of the first to point out, about the middle of the last century, the dangers accompanying the use of methyl alcohol in industrial plants. Since then many authentic cases of poisoning, due to the inhalation of the vapour, have been reported.[2,3,4] The fatalities have occurred chiefly among workmen who have been in vats or in other extremely confined spaces and who have breathed vapours arising by evaporation from large varnished surfaces. Very severe cases have been reported amongst hat finishers and wood polishers. Although the dangers arising from the ingestion of wood alcohol have been known for a considerable time, the effects of its inhalation have not been adequately studied. Coupled with the fact that absorption through the skin may present a possible danger, it is apparent that slight exposures are potential health hazards. In man, individual susceptibility and cumulative effects, together with lack of quantitative data concerning its action within the body, prevent a statement as to a definite minimum toxic concentration being made.

Loewy and von der Heide[5] state that inhalation, for a sufficiently long time, of 200 parts per million in the air, leads to harm in animals. When they made a survey of workrooms where methyl alcohol was used, they found concentrations in the air varying between 50 and 600 parts per million. It has been reported[6] that 200 parts per million were found in the atmosphere in a factory for making artificial flowers at a distance of two metres from the point where the dipping was done. McCord,[7] from his experiments on rats, rabbits and monkeys, concludes that the threshold of danger by inhalation is well below 1000 parts per million, and that if this degree of concentration applies to man, the vapour of one ounce of methyl alcohol entering the human body constitutes a threat to life when the exposure is distributed over two or three days. As low concentrations seriously affect the health of monkeys, it is apparent that a real danger exists when methyl alcohol is used even in small quantities over a long period of time, when no precautions are taken. It has been suggested[8] that ventilation should be required when 1 part per 10,000 is found in the air. This concentration can easily be attained in industrial exposures as a result of rapid evaporation from large surfaces and from open tanks, especially when such operations are carried out without adequate ventilation.

Synthetic methyl alcohol has been shown to exhibit toxic properties comparable with those obtained from wood alcohol made by the distillation process. Whatever the effect of the impurities present in the distilled product, there appears to be no question as to the toxicity of methyl alcohol *per se*.

Although many methods for the determination of small amounts of methyl alcohol have been suggested, the most sensitive test is that based upon the oxidation of the alcohol to formaldehyde and the subsequent determination of this product by means of Schiff's reagent (fuchsine or rosaniline in sulphurous acid). The use of this reagent for the estimation of small amounts of methyl alcohol was first proposed by Denigès,[9] and the method was subsequently improved by numerous investigators.[10,11,12,13,14,15,16] The original test and the modifications were developed for the determination of methyl alcohol in alcoholic beverages, extracts and medicinal tinctures, all of which contain large amounts of ethyl alcohol. Acetaldehyde, resulting from the oxidation of the ethyl alcohol, produces a colour with Schiff's reagent and thus acts as an interfering substance. Conditions under which no colour is developed from relatively large quantities of acetaldehyde seriously affect the amount of colour produced from the formaldehyde. Thus the presence of large amounts of ethyl alcohol in the solutions to be analysed greatly decreases the sensitivity of the test. In determining the concentrations of methyl alcohol vapour in air, this difficulty does not arise, as the tests are made on aqueous solutions. Obviously, these aqueous solutions will contain minute amounts of ethyl alcohol if its vapour is present in the air.

Preliminary experiments showed that methyl alcohol vapour can be removed quantitatively from air by bubbling the air through water. The method used for the collection of samples will be described in detail in a later communication. When the amount of alcohol collected by passing the air through water is very small, the alcohol can be concentrated by distillation. This method, however, is tedious when a large number of samples are being analysed, and in such cases it is often preferable to use larger volumes of the original air.

EXPERIMENTAL.—The method is as follows:—Ten ml. of the methyl alcohol solution is oxidised with acid permanganate in the presence of small amounts of ethyl alcohol. The excess of permanganate is reduced with oxalic acid, the acidity is adjusted by the addition of sulphuric acid, and the colour is developed with Schiff's reagent. The test is carried out in a 25-ml. measuring flask. As the conditions have a marked influence on the production of formaldehyde and the final colour intensity, each step in the procedure was studied in detail.

Preliminary experiments with formaldehyde showed that the production of colour depends upon the hydrogen ion concentration of the solution in which the colour is developed. Too high or too low acidity decreases the amount of colour obtained. The hydrogen ion concentration resulting from the addition of 0·6 ml. of concentrated sulphuric acid, just before the introduction of the Schiff's reagent, gave the best results. The colours obtained from 10 ml. of solutions containing as little as 8 parts per million of formaldehyde can be compared in a colorimeter. By looking lengthwise through a test-tube against a white background and comparing with a blank, the limit of detection is of the order of 1 p.p.m. of formaldehyde.

Practically no formaldehyde is formed when very dilute solutions of methyl alcohol are oxidised with acid permanganate in the absence of ethyl alcohol. This oxidation can be aided and the production of formaldehyde increased by the addition of small amounts of ethyl alcohol to the 10 ml. of methyl alcohol solution used in the test. The two alcohols are oxidised simultaneously. The possibility of obtaining formaldehyde from the ethyl alcohol is avoided by carrying out the oxidation at a low acidity. Obviously, only a little ethyl alcohol can be used, as large amounts of acetaldehyde give a colour with the Schiff's reagent. It was ascertained that 0·6 ml. of concentrated sulphuric acid is just sufficient to prevent any colour being developed from the acetaldehyde produced through the oxidation of 0·05 ml. of ethyl alcohol.

The amount of potassium permanganate added is very important, as it is one of the chief factors which controls the amount of formaldehyde formed. Five ml. of 2 per cent., 1 per cent., and 0·5 per cent. potassium permanganate solutions were used. The first two gave equally good results. With the third the amount of colour obtained was reduced very considerably. As a large excess of the oxidising agent seems unnecessary, and as it requires additional quantities of oxalic acid for decolorisation, 5 ml. of the 1 per cent. solution were chosen as the desired amount.

In the original paper of Denigès the oxidation of the two alcohols was carried out in the presence of sulphuric acid. Later it was shown that a low hydrogen ion concentration tended to increase the amount of formaldehyde formed, and at the same time decreased the production of acetaldehyde. For this reason the use of phosphoric acid was suggested. As the amount of acid added is very important, various quantities of 85 per cent. phosphoric acid were tried. It was found that a minimum concentration of acid gave the best results; 0·25 ml. of 85 per cent. phosphoric acid produced a desirable acid concentration, with a consequent slow rate of oxidation. The length of time necessary for the optimum oxidation at room temperature was not definitely determined, but an interval of one hour was deemed sufficient.

The quantity of oxalic acid added seems to have little effect on the final colour production. Only the amount to reduce the excess potassium permanganate is necessary. This reduction is effected within a few minutes by the use of 1 ml. of a 5 per cent. solution.

Originally, Schiff's reagent was prepared by dissolving fuchsine in water and decolorising the solution by the addition of sulphurous acid. Subsequently, many different modifications were suggested. The use of sulphurous acid has been discontinued, as it is more convenient to add sodium sulphite or bisulphite and mineral acid directly to the solution of the dye. Recently fuchsine has been replaced by rosaniline, as it is claimed that the latter gives a more stable reagent. However, throughout these experiments we used fuchsine and found it to be entirely satisfactory.

Our Schiff's reagent, when kept at room temperature in a well-corked brown glass bottle, was stable for at least three months. Indeed, its sensitivity gradually increased, possibly owing to a slow loss of sulphur dioxide. The fact that a low concentration of sulphurous acid increases the sensitivity of the Schiff's reagent has been observed by others.

REAGENTS.—The following reagents are required:—Standard methyl alcohol solutions; 5 per cent. (vol.) ethyl alcohol solution; 1 per cent. potassium permanganate solution; phosphoric acid (85 per cent.), 25 ml. made up to 100 ml. with water; 5 per cent. oxalic acid solution; sulphuric acid, 30 ml. of concentrated acid made up to 100 ml. with water.

Schiff's Reagent.—Grubler's fuchsine (0·5 g.) is dissolved in 400 ml. of warm water. After cooling, 2 g. of anhydrous sodium bisulphite are added, and the solution is stirred until the salts are dissolved, after which 4 ml. of concentrated sulphuric acid are added, with stirring, and finally the solution is transferred to a brown glass bottle and securely corked. It is allowed to stand over-night, after which the reagent should be colourless.

METHOD.—Ten ml. of the methyl alcohol solution are pipetted into a 25-ml. graduated flask, and 1 ml. of dilute ethyl alcohol, 5 ml. of potassium permanganate and 1 ml. of dilute phosphoric acid are added. The oxidation is allowed to proceed at room temperature for one hour with occasional gentle shaking. One ml. of oxalic acid solution is then added and the flask is shaken again. When the solution has become colourless or nearly so, 2 ml. of dilute sulphuric acid are added, followed by 5 ml. of Schiff's reagent, and the solution is mixed by inverting the flask two or three times. After standing for three hours, the solution is compared in a colorimeter with a standard methyl alcohol solution prepared at the same time and in the same way.

DISCUSSION.—When different amounts of a standard methyl alcohol solution are treated with the reagents, the depth of colour produced is not proportional to the concentration. When the relative intensity of colour is plotted against the concentration, a curve is obtained the shape of which is not always the same, but depends upon the time allowed for the colour development. Solutions containing 500 parts per million of methyl alcohol reach their maximum colour intensity within one hour. Solutions containing 30 parts per million need at least three hours. It has been claimed that the colour fades rapidly, and that the solutions must be compared within a few minutes. We have found, however, that the colour is fairly stable, and that with the stronger solutions many days elapse before the colour finally disappears.

It is found that the section of the graph lying between 100 and 250 p.p.m. is approximately a straight line. When extended, this line does not pass through the zero. It is best, however, to carry out the determinations on methyl alcohol solutions which have a concentration lying within this range.

A concentration of about 30 p.p.m. is the lowest suitable for quantitative comparison in a colorimeter. For purely qualitative work the minimum limit of detection approximates to 5 p.p.m.

It is quite obvious, from a comparison of the colours produced by standard methyl alcohol and formaldehyde solutions, that the conversion of the methyl alcohol into formaldehyde is not quantitative. It has been pointed out that this reaction depends upon the concentration of both the permanganate and acid during the oxidation. Also, it was found that relatively more formaldehyde is obtained from the oxidation of weak than from that of strong alcoholic solutions. Quantitative experiments showed that when solutions containing 250 p.p.m. of methyl alcohol were oxidised by the method described above, the quantity of formaldehyde produced was only about 14 per cent. of the theoretical amount. As weaker solutions are tested, the percentage steadily rises, and from solutions containing 30 p.p.m. the yield is 19 per cent. This is one of the reasons why the final colour intensity is not proportional to the concentration. Furthermore, different standard formaldehyde solutions do not produce a corresponding proportionality of colour. This is most apparent when weak solutions are tested, as different colours are produced. The colour-change obtained from solutions containing decreasing amounts of formaldehyde is magenta, purple, blue-purple, blue, and finally grey.

When the conditions of the test are adhered to rigidly, parallel determinations agree very closely; nevertheless, an appreciable error may be introduced unless the experiments are performed in triplicate. Furthermore, the varying colours produced by different amounts of formaldehyde necessitate the unknown solution being compared with a standard having approximately the same concentration of methyl alcohol. By observing these conditions the error of the test is less than 5 per cent. In determining the quantity of methyl alcohol vapour in the air, a greater accuracy than this is unnecessary.*

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The Composition of Raspberries

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EVER since the Jam Standards were agreed upon there have been suggestions that the composition of Scotch raspberries was different from that of the English fruit, particularly in the percentage of seeds and fibres (insoluble matter). An opportunity occurred last season to secure samples of both Scotch and English fruit for analysis. Mr. Adamson, of Blairgowrie, very kindly undertook to collect samples of raspberries throughout the whole of the season, sending them to the Research Association by passenger train.

The arrangements made with Mr. Adamson were carried out without a hitch, and the fruit was found to be in sound condition on arrival at the Association's laboratories. Messrs. Chivers also undertook to send samples of the same varieties of raspberries from their orchards in Cambridgeshire and in Scotland. They also collected samples from the Forfarshire district.

The results of the analyses and all particulars are given in the following table:

TABLE I

Source	Variety	Weather conditions	Insoluble solids Per Cent.	Seeds per 100 g.		Soluble solids Per cent.	Free acid (as hydrated citric acid) Per cent.
				Number	Weight		
Adamson, Blairgowrie	Lloyd George	Dry.	4·48	2870	3·43	—	—
,,	,, ,,	Bushes dry. No rain for 24 hrs., but previously rain at intervals. Ground moist.	5·14	3355	4·14	—	—
Chivers, Histon	,, ,,	Extremely dry.	4·95	4130	3·86	12·0	1·60
,, ,, "X"	,, ,,	,, ,,	5·15	5000	3·89	12·2	1·80
,, Oakington (1)	,, ,,	,, ,,	5·44	5470	4·29	10·9	1·55
,, ,, (2)	,, ,,	,, ,,	5·18	4360	4·14	11·05	1·70
Adamson, Blairgowrie	,, ,,	Rain 22 July. Picked 23rd, but bushes dry then.	4·87	3350	3·92	7·25	1·50
Chivers, Arbroath	,, ,,	Showery, following sunny day.	5·30	3570	3·76	6·5	1·89
Chivers, Brechin	,, ,,	,, ,, ,,	5·93	4500	4·70	6·8	1·78
Chivers, Lunan	,, ,,	,, ,, ,,	5·92	4590	4·62	6·8	1·84
Chivers, Montrose	,, ,,	,, ,, ,,	6·20	4600	4·82	6·7	1·78
Adamson, Blairgowrie	,, ,,	Some rain previous night, fruit quite dry when picked.	4·66	3390	3·80	6·7	1·38
Chivers, Edzell	Devon	Sunny day.	6·77	4190	5·02	8·45	1·56
,, ,,	Lloyd George	,, ,,	5·16	3810	4·02	9·2	2·50
Adamson, Blairgowrie	Mitchell's	No rain for 12 hrs. before picking. Bushes and fruit quite dry.	4·41	2390	3·10	8·2	1·43
Chivers, Brechin	Devon	Showery weather.	5·54	3015	4·26	7·15	2·13
,, ,,	Mitchell's	,, ,,	6·10	3590	4·65	7·5	1·82
,, ,,	Antwerp	,, ,,	5·16	3705	3·93	8·8	1·47
Adamson, Blairgowrie	Lloyd George	Heavy rain for 24 hrs., but bushes allowed to dry for about 5 hrs. before picking.	3·84	3100	3·14	7·9	1·45
,, ,,	Mitchell's	No rain for 2 or 3 days.	4·54	3400	3·41	7·8	1·66
,, ,,	Lloyd George	No rain for several days.	3·91	3320	3·04	7·4	1·52
,, ,,	,, ,,	No rain for more than a week.	3·62	2990	2·85	9·1	1·77
,, ,,	,, ,,		3·29	2935	2·38	10·0	1·93
,, ,,	,, ,,		3·31	3175	2·52	10·1	1·75
1934.	Highest (Scottish fruit)	.. ..	6·77	4600	5·02	10·1	2·50
	Lowest ,, ,,	.. ..	3·29	2390	2·38	6·5	1·38
	Average ,, ,,	.. ..	4·91	3490	3·78	7·91	1·73

It will, no doubt, be remembered that drought conditions existed in England during July, when the English raspberries were in season. On the other hand, conditions as regards rain were normal in the Scotch districts, except after the second week in August when no rain fell for over ten days. The claim has frequently been made that Scotch raspberries must contain more water, and consequently less fibre and soluble solids, than the English fruit, as the result of the wetter climate.

If we now examine the results given above, keeping in mind the different weather conditions, it will be apparent that wet or dry conditions have no definite influence on the quantity of insoluble solids (seeds and fibre). Thus, the raspberries from Blairgowrie (July) contained from 4·48 to 5·14 per cent. of insoluble solids. Those from Cambridge taken about the same period contained 4·95 to 5·44 per cent., and those from the Forfarshire areas from 5·3 to 6·2 per cent. On the other hand, the fruit ripening later in the season (August 9th to August 21st) contained a gradually decreasing amount of insoluble matter, *viz.* from 3·91 per cent. down to about 3·3 per cent.—the lowest figure so far recorded for this constituent. Yet the weather at this period was dry. These results all apply to the Lloyd George variety.

It will be obvious, from these comparisons, that the wetness or dryness of the climate has little or no influence on the amount of insoluble matter in the fruit. This would appear to be dependent, first, on the variety of raspberry; secondly, on soil or other horticultural factors, such as age of cane; and thirdly, on the length of time the fruit is on the cane. This last influence would appear to be the most important factor in lowering the percentage of insoluble solids. It would seem, judging by the results obtained with the raspberries picked in mid- and late-August, that the fleshy part of the fruit then develops to a greater extent than in the earlier fruits, the ratio of weight of seeds to juice being thus lowered.

If the numbers of seeds per 100 g. of fruit are compared, it will be seen that the Blairgowrie fruit has fewer seeds than that grown either in Cambridgeshire or Forfarshire, though in the early part of the season they are evidently larger on the whole, as the number per gram varies from about 800 to 1000, compared with 1000 to 1280 for Cambridge fruit. In the late season, however, both number and size of seeds apparently decrease.

It is only when the soluble solids are considered that the influence of climate becomes more obvious. The fruit grown in Cambridge contained from 10·9 to 12·2 per cent., whilst that from both Scotch areas contained from 6·5 to 9·2 per cent.

These differences are more probably due to the influences of sunshine in developing the sugar in the Cambridge fruit rather than to the dilution of the juice of the Scotch fruit through growing under moist conditions. It should be noted that in the fruit collected late in August the soluble solids increased from 7·4 to 10·1 per cent., whilst the insoluble solids decreased from 3·91 to 3·31 per cent. These facts are in accordance with the theory that both are due to ripening changes.

One fact worthy of note is that the acidity remains remarkably uniform throughout the whole series and does not seem to be influenced by soil, climate or other factors. Except in three samples, the acidity ranges between 1·5 and 1·9 per cent., the majority of the results lying between 1·6 and 1·8 per cent.

The very low insoluble-solids figure obtained here increases the difficulties of the analyst who has to determine the fruit-content of a jam, but, if the acidity figure is also considered along with that for the soluble solids, the difficulty can be overcome to a considerable extent.

A very important consideration in connection with the drafting of standards for manufactured foodstuffs is raised by the results of this series of analyses. It is generally agreed that it is valueless to set up standards for any product, unless their maintenance can be assured by analysis or other suitable means.

If they are to be maintained by analysis, then the limits of variation in the composition of the natural products used in making the foodstuffs must be carefully determined. The difficulty of arriving at the extreme limits occurring naturally is well illustrated by the results of the investigation into the composition of raspberries carried out by the Research Association.

The following table shows the number of samples analysed during different periods with the corresponding variations in composition.

TABLE II

Period	No. of samples	Insoluble solids, per cent. Min.	Max.	Average
1923–24	7	6·4	8·55	7·59
1925	12	4·7	9·2	6·45
1926	15	4·9	8·7	6·09
1927	20	4·4	6·7	5·58
1929	8	5·6	8·3	6·70
1934	23	3·29	6·77	4·91

From this table it will be seen that over 80 samples were examined before the lowest limit, so far recorded, was found. There is, therefore, a possibility that samples of raspberry jam, which have been reported as deficient in fruit on the basis of the insoluble-solids figure, may not have been deficient at all.

While all natural products may not vary in composition to the same extent as raspberries, they certainly vary widely enough to make it difficult for an analyst to determine within reasonably narrow limits the proportion of any of them contained in a manufactured product. This is certainly true of meat and fish products, the composition of which will require verification by a much larger series of analyses than have been recorded so far.

It is to be hoped, therefore, that before legal standards for manufactured food products are enforced the necessary limits will have been determined by a very comprehensive series of analyses, which should cover all varieties of the particular natural product under all conditions of growth.

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The Application of the Furfural Test for Mint Oils to Other Essential Oils

By D. C. GARRATT, B.Sc., Ph.D., F.I.C.

Since the introduction of the furfural test (Analyst, 1935, 369) for the detection of Japanese mint oil in peppermint oils, a number of commoner essential oils have been examined by the same method in order to determine whether the test might have extended application. The results as shown in Table I were obtained.

La Wall (*Amer. J. Pharm.*, 1920, 92, 891) had noted the presence of furfural in wintergreen oils (*Gaultheria* and *Betula*), whereas methyl salicylate contained none, but he was of the opinion that for mixtures the reaction was valueless, as its application was easily defeated by the addition of a little furfural. This is obvious and, for the detection of, say, Australian in Mysore sandalwood oil the reaction would be of little use. But if the adulterant has a relatively much higher furfural-content, the method becomes applicable, as it is much more difficult to free an oil from furfural, and only specially prepared oils could be used.

TABLE I

	10-Min. red value		10-Min. red value
Ajowan	4·1	Geranium (French)	0·4
Almond	0·0	Gingergrass	1·9
Aniseed (star)	5·6	Juniper berry	0·2
Bay	1·4	Lavender (French)	0·9
Bergamot	0·1	Lavender spike	1·2
Cajuput	0·2	Lemon	0·1
Camphor (brown)	0·3	Lemongrass	29·5
Camphor (light)	9·2	Neroli	1·7
Cananga	2·5	Nutmeg	0·2
Caraway	0·6	Orange	0·2
Cassia	5·8	Palmarosa	0·9
Cedarwood	0·0	Pennyroyal	7·9
Chenopodium	0·5	Petitgrain	5·5
Citronella (Ceylon)	2·4	Pimento berry	1·1
Citronella (Java)	0·3	Pine (pumilio)	0·5
Cinnamon bark	3·7	Rose (French)	1·0
Cinnamon leaf	1·7	Rosemary	0·8
Clove	23·0	Sandalwood (Australian)	0·9
Copaiba	0·1	Sandalwood (Mysore)	11·0
Coriander	0·4	Savin	0·2
Cubebs	0·5	Siberian Fir	0·5
Dill	0·6	Spearmint	1·1
Eucalyptus	3·3	Thyme (red)	9·0
Eucalyptus (Dives)	2·1	Turpentine	0·4
Eucalyptus (Citriodora)	1·4	Wormseed	0·4
Geranium (Algerian)	0·6	Ylang-Ylang	2·3
Geranium (Bourbon)	0·4		

(Wintergreen and sassafras oils were not available. Neither methyl salicylate nor safrol gave a red value.)

From consideration of Table I, the usefulness of the reaction for the detection of light camphor oil in rosemary, and clove oil in bay or pimento berry was apparent, and a few experiments were made to show the possibilities of the test.

My thanks are due to M. J. H. Moutet, of Grasse, for authentic specimens of French and Spanish rosemary oils; the other Spanish oils used were kindly given by Mr. C. E. Sage from samples passed by him as genuine. These oils gave the figures shown in Table II.

TABLE II

	10-Min. red value
French rosemary (Moutet)	0·4
Spanish „ „	0·4
„ (C. E. Sage) 1	0·5
„ 2	0·5
„ 3	0·7
„ 4	0·8
„ 5	0·4

Thus all show a fairly consistent low red value.

The results given by samples of light camphor oil, bought commercially, are shown in Table III.

TABLE III

	Sp.gr.	Opt. Rotn.	Cineole Per Cent.	10-Min. red val.	Odour
Light camphor oil A	0·8880	+19°40′	30·0	9·2	cineole and terpenes
,, ,, ,, B	0·8870	+25°10′	22·4	8·5	cineole and camphor
,, ,, ,, C	0·8935	+11°5′	42·6	5·0	cineole
,, ,, ,, D	0·8985	+12°0′	44·0	4·1	camphor and cineole
,, ,, ,, E	0·8985	+ 7°10′	32·8	3·6	cineole and terpineol
,, ,, ,, F	0·8955	+11°30′	45·8	3·3	strong cineole
,, ,, ,, G	0·8985	+12°10′	44·8	1·8	cineole and camphor
,, ,, ,, H	0·9470	+ 2°0′	29·4	0·6	safrol (abnormal oil)
,, ,, ,, I	0·8825	+ 2°0′	7·0	0·0	strong terpineol and safrol

On consideration of the above figures it will be seen that the most suitable oils for the adulteration of rosemary oil, having regard to the physical constants, would be C to G inclusive. These oils would increase the red value of rosemary appreciably, as they have a relatively higher furfural-content; hence the application of the test to detect this adulterant should be useful.

By the courtesy of Mr. W. A. N. Markwell, of Messrs. Potter & Clarke, samples of genuine clove oil were obtained, and these gave the following values (Table IV):

TABLE IV

Clove oil			10-Min. red value
From Zanzibar buds (i)	distilled by steam under pressure	..	23·0
,, ,, ,, (ii)	,, ,, ,, ,, ,,	..	22·0
,, ,, ,, (iii)	,, ,, ,, ,, ,,	..	22·0
,, ,, ,, (iv)	,, ,, ,, ,, ,,	..	22·5
,, ,, ,, (v)	steam-distilled in laboratory	..	4·6
From Penang buds (vi)	,, ,, ,, ,,	..	10·0

The high value for the oils produced by large-scale manufacture is probably normal, as it is well known that clove oil has a very high furfural-content (Schimmel's Reports, 1902, p. 24), and samples bought commercially gave similar values.

As bay and pimento oils gave values of 1·1 and 1·4, respectively, the inclusion of clove oil would easily be detected. When 10 per cent. of clove oil (i) was added to pimento oil, and subjected to the test, the colour could not be matched on the Lovibond tintometer (B.D.H.), as both red and yellow values were above 10.

When the above clove oils were diluted ten times with glacial acetic acid and the red value measured on 0·1 ml. of the dilution, the values obtained were 14·9, 14·5, 15·3, 14·5, 0·4, 1·0, respectively; hence the red values at higher concentrations are not a linear function of the concentration of furfural.

The test is offered tentatively as an added means for the detection of adulteration; only time and experience with a large number of oils will determine its usefulness.

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The Electrolytic Determination of Lead as Dioxide and its Conversion into Lead Monoxide by Ignition

By A. J. LINDSEY, M.Sc., A.I.C.

LEAD dioxide, as electrolytically deposited, contains water that cannot readily be driven off by heating. Most analysts have adjusted the conditions of deposition and drying so that the amount of water in the deposit is constant and have employed a factor (differing slightly from the theoretical ratio Pb/PbO_2) to obtain the correct amount of lead.[1,2,3,4]

Treadwell[5] recommends that the deposit of lead dioxide in a platinum dish be heated gently over a flame to convert it into lead monoxide, which is then weighed. This procedure is obviously inapplicable to lead dioxide deposited upon gauze electrodes, since the reducing gases in the flame would produce lead, which would then alloy with the platinum.

The present experiments were made to ascertain whether the method would yield satisfactory results with gauze electrodes if electrical heating were employed.

TABLE I

Lead taken g.	Lead dioxide found g.	Lead calc. (factor, 0·8635) g.	Lead monoxide found g.	Lead calc. g.	Time in furnace. Min.
0·2834	0·3281	0·2833	Deposits not ignited		
0·2834	0·3276	0·2829			
0·2834	0·3278	0·2831			
0·2834	0·3281	0·2833			
0·2834	Lead dioxide not weighed		0·3046	0·2830	5
0·2834			0·3021	0·2804	5
0·2834			0·3026	0·2809	5
0·3678	0·4248	0·3668	0·3901	0·3621	5
0·3678	0·4256	0·3676	0·3895	0·3616	5
0·3678	0·4258	0·3678	0·3933	0·3653	2
0·3678	0·4252	0·3672	0·3910	0·3629	2
			0·3875	0·3597	10
			0·3857	0·3581	15

A vertical electric tube furnace was therefore constructed in which the gauze electrode previously described[6] was hung by a nichrome wire hook. The temperature was adjusted to 700° C., the following considerations having led to this choice of temperature.

Lead monoxide melts at about 830° C., and is slightly volatile at this temperature. (At 700° C. it is said to lose 0·1 per cent. of its mass per hour, and at 800° C. 0·2 per cent.)[7] At temperatures below 500° C. lead monoxide, in presence of air, forms red lead.[8]

The time necessary for the complete conversion of the lead dioxide into monoxide was found to be from two to five minutes. The determinations (Table I) were made, using the method of deposition described by Collin,[4] and the apparatus devised by Sand.[9] Before the electrolyses were terminated a portion of the electrolyte was withdrawn by means of a pipette, made alkaline with ammonia, and tested with hydrogen sulphide solution for lead. The factor (0·8635) used for the calculation of the lead from the lead dioxide found is that determined by Collin.[4]

The preceding results show that the lead monoxide found was in every case low. Moreover, repeated ignition caused a continuous decrease in weight, due, no doubt, to volatilisation of the oxide.

To confirm this, lead dioxide was deposited upon a platinum dish, as recommended by Treadwell, and then ignited. Two determinations were made.

TABLE II

Lead taken g.	Lead dioxide found g.	Lead calc. (factor, 0·8635) g.	Lead monoxide found g.	Lead calc. g.	Time of heating Min.
0·3678	0·4240	0·3662	0·3922	0·3641	1
0·3678	0·4233	0·3658	0·3904	0·3624	1
			0·3891	0·3612	2
			0·3880	0·3601	3

It will be noted also that when a dish is employed, the results for lead oxide are low and decrease continuously on heating. Another objection inherent in ignition lies in the resistance offered by the ignited oxide to removal by dilute nitric acid. When the gauze electrodes were employed it was found best to dispense with complete removal of the deposit between successive experiments in a series. Complete removal of the deposit by electrolytic reduction, followed by treatment with boiling nitric acid, led to appreciable loss of platinum. The ignition of lead dioxide deposits to lead monoxide is therefore not recommended.

I wish to express my thanks to Dr. H. J. S. Sand for his suggestions and interest in this work.

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A Study of Heat Exchange in the Cryoscopes of Hortvet and Monier-Williams for the Determination of the Freezing-Point of Milk

By J. R. STUBBS, M.Sc., F.I.C.

(Communicated through the North of England Section)

In a previous paper[1] the supercooling and heat-transference factors have been defined, and a description has been given of an attempt to obtain them with the standard Hortvet cryoscope, modified only sufficiently to permit of the withdrawal of alcohol from the jacket surrounding the freezing-tube. It was there shown that the methods employed for the determination of these two factors will give values which can only be regarded as accurate if, when the alcohol is removed, the milk (including those portions of the apparatus which participate in this heat exchange) suffers neither nett gain of heat from, nor loss to, its surroundings during the rise of temperature while freezing is in progress; if, during that time, there is not thermal equilibrium, the values of both these corrections will be affected.

It was proved that, when the alcohol is removed, there is still a transference of heat in the Hortvet apparatus across the annular space surrounding the freezing-tube, the amount of this heat being greater than that which finds its way in from the atmosphere or other sources; a determination of the freezing-point may be carried out without the use of alcohol, or indeed, of any liquid at all in this space; but if this is done, the nett amount of heat lost by the freezing-tube and contents in a unit of time is less than when the alcohol is allowed to remain and, consequently, the time required to cool the milk is prolonged. In one experiment a milk was cooled from 0° to —1·70° in about 4 minutes when using alcohol, compared with about 24 minutes when no alcohol was present. The removal of alcohol in the standard Hortvet apparatus does not abolish, but only reduces, the heat transference from the freezing-tube to the cooling-bath maintained at —3·0°.

It should be clearly borne in mind that the Hortvet apparatus was not designed with a view to the determination of the supercooling and heat-transference factors; Hortvet claimed that these corrections might be left undetermined and still, if his standard apparatus and technique were invariably adopted, the simplified procedure would yield results which would be satisfactory for all the practical purposes for which the freezing-point test is applied to milk.

Monier-Williams[2] described a new form of apparatus designed by himself. He stated that by its use the correction factors of supercooling and heat exchange could be determined, and by the application of these corrections to the observed freezing-point, the true freezing-point could be ascertained. The experience with the Hortvet apparatus, just described, that is, the interference caused by a nett loss of heat suffered by the freezing-tube and milk when no alcohol was used, suggested an enquiry into the position of the Monier-Williams cryoscope in this respect under similar circumstances.

The following observations were made mainly in connection with the elucidation of this point and, for comparison, similar work was undertaken with the modified Hortvet cryoscope.[3] The later model of the Monier-Williams apparatus[2] was used.

I. THE COOLING BATH.—The cooling-bath of each type of apparatus consists of a vessel containing ether through which a regulated current of air is passed. The control thermometer supplied with the Monier-Williams cryoscope had too close a scale to enable fractions of a degree to be estimated satisfactorily, so it was decided to use the more open scale thermometer, supplied with the Hortvet apparatus, in all experiments. It was found far from easy to maintain a strictly, as distinct from an approximately, uniform temperature of the cooling-bath. The sources from which it receives heat are the atmosphere and the freezing-tube with its contents; the quantity of heat received from these sources varies as the temperature of the milk falls, rendering necessary a frequent adjustment of the rate of passage of air through the ether.

The Dewar flask of the Hortvet apparatus is a very efficient heat insulator, and it might be thought that a continuous current of air would be unnecessary, for, if it is stopped, the thermometer in the cooling-bath remains at —3·0° for some time, while the cooling of the milk still continues. But in a series of experiments, made with the object of ascertaining the rate of fall in temperature of the contents of the freezing-tube, it was observed that when no current of air was passing, although the control thermometer registered —3·0°, the rate of cooling of the milk diminished considerably; if the air current were then started, the thermometer rose sometimes by 0·5°, or even 0·7°, and, on adjusting the temperature by means of the air current to —3·0° again, the rate of cooling of the milk increased at once.

It would appear that, in the absence of a continuous current of air sufficient to keep the ether mixed, a layer of comparatively warm ether forms in the bath on the exterior of the metal tube, and that this protects the milk, so that it does not receive the full cooling effect due to a cooling-bath temperature of —3·0°.

In the experiments described in this paper where the liquid in the freezing-tube was cooled to a temperature of about —2·3°, it was found very difficult to maintain an air current which was sufficiently slow to prevent the temperature of the cooling-bath from falling below —3·0°, and, on the other hand, strong enough to serve for thorough mixing of the ether.

In the Monier-Williams apparatus the cooling-bath is a thin brass vessel embedded in a block of cork. Cooling is a longer process than with the Hortvet apparatus—usually at least two or three times as long. A continuous current of air is necessary to keep the temperature as low as —3·0°. If, in the endeavour to expedite the cooling, the rate of the air current is increased, liquid ether is liable to be carried away. It is suggested, therefore, that it might be worthy of consideration whether the depth of the brass vessel should be increased with a view to permitting the use of a stronger current of air, thereby reducing the time needed for cooling.

The greater consumption of ether which takes place in using the Monier-Williams instrument leads to certain inconveniences, apart from the question of cost. It becomes necessary to add ether more frequently and in greater quantity than when using the Hortvet cryoscope, and, since the ether is usually at a higher temperature than —3·0°, time is lost in cooling down again, and the difficulties of maintaining a uniform temperature and the same level of ether are very great. It seems that the block of cork is a much less efficient heat insulator from the surrounding air than the Dewar flask which performs the same function in the Hortvet cryoscope.

If the air current is stopped, the temperature of the cooling-bath rises more quickly in the Monier-Williams apparatus than in that of Hortvet; this confirms the previous observation that, in the former case, the insulation from the heat of the atmosphere is less efficient.

In the Hortvet apparatus the air current has to be gradually diminished in order to maintain the cooling-bath at —3·0° as the temperature of the milk falls. If, for instance, the adjustment be made when the reading of the freezing-point thermometer is at about —1·0°, the stream of air will be found to be too rapid as the temperature of the milk becomes lower, for the temperature of the cooling-bath will fall. Experience of the care necessary to procure this adjustment of the air stream raises the suggestion in the mind that it might be well to consider whether, for critical work, two control thermometers should be used in the cooling bath, and some system provided for effective mechanical stirring independent of the current of air.

II. THE FREEZING-TUBE AND CONTENTS.—The terms "heat transference" and "heat exchange" are both applied more particularly with regard to the exchange of heat between the contents of the freezing-tube and the surroundings. In the ordinary Hortvet technique, as specified in the A.O.A.C. regulations, methylated spirit is used in the jacket around the freezing-tube, while in the case of the Monier-Williams cryoscope 15 per cent. alcohol serves as the liquid to facilitate cooling. The heat transference due to the presence of this alcohol has been studied for the Hortvet apparatus, and the factor was found by me to be 0·006,[1] while Monier-Williams found a corresponding figure of 0·009 for his own cryoscope.[2]

The work now to be described concerns the question of heat transference when the space surrounding the freezing-tube is occupied by air. The cooling-bath was, in all experiments, maintained as near to —3·0° as possible.

The temperature of the surrounding air was, in every case, about 17° C. Thirty-five ml. of milk were used in the Hortvet apparatus except when otherwise stated and 55 ml. in that of Monier-Williams; the same rise or fall of temperature, therefore, indicated that, in the latter case, more heat was involved.

The same freezing-point thermometer was used for experiments on the same milk with both cryoscopes. The work was repeated on a different milk using another thermometer. Genuine milks of average quality were used and such as by smell and acidity were shown to be quite fresh.

When the desired amount of cooling had been obtained the liquid was drawn off from the space surrounding the freezing-tube; all the following observations were therefore begun with the surfaces of the jackets in a wet state.

A rubber band round the lower part of the exterior of the Hortvet freezing-tube prevented it from coming into contact with the metal tube of the cooling-bath.

No freezing of the milk took place in any of the experiments. The Hortvet stirrer was mechanically operated at the rate of 40 up-and-down strokes per minute, and the Monier-Williams stirrer, by hand, at the rate of 1 up-and-down stroke in 2 seconds.

For the present purpose it is only necessary to consider the position during the period in which the temperature is rising from the onset of freezing until it becomes stationary, when the jacket surrounding the freezing-tube is occupied by air. Assuming that a supercooling of 1·2° is used, this will correspond to a reading of the thermometer of about —1·74°, and the highest temperature reached will be the observed freezing-point of the milk, *viz.* about —0·54°; that is, we are concerned only with the interval between —1·74° and —0·54° on the thermometer fitted to the freezing-tube.

(1) *Consideration of residual heat transference commencing with the milk in the freezing-tube at about* —0·54°. (*Temperature of cooling-bath* —3·0°.)

(*a*) With the Hortvet apparatus:—The temperature fell gradually by decreasing amounts per unit of time, and at —1·74° was still falling, showing that the milk was still undergoing a nett loss of heat.

(*b*) With the Monier-Williams apparatus:—The temperature fell at first, but, after a time, a point was reached when the position of the mercury became stationary at —0·83° and —0·93°, respectively, in two experiments.

(2) *Residual heat transference commencing with the liquid in the freezing-tube at about* —1·74°.

(*a*) With the Hortvet apparatus:—The temperature fell in small, but quite appreciable, amounts.

(*b*) With the Monier-Williams apparatus:—The temperature gradually rose and attained in two experiments temperatures of —1·2° and —1·4° respectively, and at the time of the conclusion of the experiments was still rising slowly.

When milk is cooled below —1·74° there is great liability to spontaneous freezing. Experiments were therefore continued with the Hortvet apparatus, using, in the freezing-tube, 15 per cent. alcohol, instead of milk. It was then found that the stationary temperature in this alcohol was —2·28° and —2·33°, respectively, in two experiments.

(3) *Conclusions from the above results.*

In an experiment for the determination of the freezing-point of a liquid, the contents of the freezing-tube are subject to two opposing influences so long as no freezing takes place, *viz.* addition of heat from the atmosphere by conduction through the freezing-tube, thermometer and stirrer, together with the heat generated by stirring, and abstraction of heat due to the action of the cooling-bath. If the cooling-bath is maintained at a constant temperature, these two influences will sooner or later balance each other, and the milk will assume a constant temperature which is called the *temperature of convergence*; exactly as much heat is then gaining access to the freezing-tube and contents as is being removed by the cooling-bath.

The above experiments, then, indicate that in the case of the Hortvet apparatus, with an air-jacket round the freezing-tube and the cooling-bath at —3·0°, the convergence temperature is about —2·3°, while in the Monier-Williams cryoscope under similar conditions it is about —0·9°. A significant point in relation to these two results is that with the Hortvet instrument the convergence temperature is *always* below any point at which supercooling is usually arrested and crystallisation is induced, while, on the other hand, with the Monier-Williams process the convergence temperature lies between the usual temperature of supercooling (about —1·74°) and the observed freezing-point. The significance of this will be discussed later in the paper.

The following remarks with regard to convergence temperatures may help to make the subject clear.

The cooling-bath has no effect on the freezing-point of the liquid under observation if the convergence temperature coincides with the observed freezing-point. Raoult[4] stated that, if they differ, the influence on the freezing-point could be taken, with a high degree of approximation, as directly proportional to the difference between the convergence temperature and the observed freezing-point; if the convergence temperature is below the observed freezing-point, the correction to be applied to the observed freezing-point depression to give the true freezing-point depression, is negative; if above, the correction is positive.

In the same apparatus, when the convergence temperature is below the observed freezing-point, if we diminish the amount of heat abstracted per unit of time, the convergence temperature will come nearer to the observed freezing-point. When these two temperatures coincide, the freezing-tube and contents are in thermal equilibrium with their surroundings. If the cooling-bath is kept at a constant temperature, the greater the difference between the convergence temperature and the temperature of the cooling-bath, the greater is the amount of heat gaining access; the bulk of this heat will be derived from the atmosphere; a certain, though a very small, part only will be due to that generated by stirring where the stirring is at a comparatively slow rate, as is the case in the technique of the two methods now under consideration.

With different apparatus, and particularly with different designs of cryoscopes, the convergence temperature corresponding to the same temperature of the cooling-bath may be expected to vary.

The difference between the convergence temperature and the observed freezing-point is greater in the modified Hortvet (*viz.* about 1·8°) than in the Monier-Williams process (about 0·4°). Raoult[5] (p. 11) has shown that if heat is abstracted while the temperature of the milk is rising during freezing, to obtain the true freezing-point depression a negative correction must be applied to the observed freezing-point depression and a positive correction if heat is added. In the Hortvet apparatus, with an amount of supercooling of milk not greater than about 1·8°, the correction will always be a negative one. For the Monier-Williams instrument the correction will be negative if the supercooling does not exceed about 0·4°, and when the supercooling is more than about 0·4°, which is usually the case in making determinations on milk, the correction will be first positive until the convergence temperature is reached, and then negative as the temperature rises to the observed freezing-point. These corrections, being of opposite sign, will tend to neutralise each other, and the correction to be applied will be the resultant of the two.*

It must follow from Raoult's formula that the observed freezing-point will be nearer to the true freezing-point with the Monier-Williams cryoscope and technique than in the case of those of Hortvet.

An idea of the approximate extent of the error in the Hortvet apparatus due to "residual" heat transference, that is, nett loss of heat when alcohol is not present, can be obtained as described below.

(1) Raoult's formula, modified so as to apply to solutions in general,[1] for obtaining the error due to reading the observed freezing-point when the convergence temperature does not coincide with it, is $\frac{C}{L}\left(H+\frac{r}{W}\right)\frac{z}{Z}$, where C is the true freezing-point depression; L the latent heat of solidification of the solvent (80 for water); H the specific heat of the liquid (0·93 for milk); r the water value of the wetted parts of the freezing-tube, stirrer, thermometer (with mercury) (6·8 in the apparatus used); W weight in grams of the liquid under examination (36); z the time taken for the temperature, while freezing is in progress, to rise from the lowest to the highest point; and Z the time required by the liquid in the freezing-tube to warm or cool 1° from the freezing-point when no freezing takes place. The quantities L, H, r, and W are constant for the same apparatus and amount of milk; if we assume that z is constant, then the factor depends on the value of Z. This time was found by experiment to be about 18 minutes in three experiments. If we assume z to be 3 minutes, then for the apparatus I used, the expression

$$\frac{C}{L}\left(H+\frac{r}{W}\right)\frac{z}{Z}=\frac{C}{80}\left(0{\cdot}93+\frac{6{\cdot}8}{36}\right)\frac{3}{18}=C\times 0{\cdot}002,$$

and the correction (negative) amounts to 0·5 × 0·002 = 0·001°.

(2) In a former paper[1] the heat-transference factor due to the presence of methylated spirit was found to be 0·006, and the time to cool from about —0·5° to —1·7° was about 3 minutes; in the absence of alcohol the time was about 18 minutes. In the above expression, L, H, r, and W, are again constant. If we assume z to be constant, then the factors will be in the inverse ratio of the values of Z, that is to say, the value of the residual heat-transference factor will be 0·006 × 1/6 = 0·001, and the correction (negative) 0·0005°.

(3) Raoult[4] gave a formula, which he claimed to be approximately correct, for the influence on the freezing-point due to the difference between the observed freezing-point and the convergence temperature, *viz.* $C' - C = Cdq$, where C' is the observed, and C the true, freezing-point depression, d is the difference between the observed freezing-point and the convergence temperature, and q a constant, which varies with solutions of different substances and of which he

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* The positive correction is very small. It is not taken into account in Raoult's equation, $C' - C = Cdq$, given later in the paper.

found the average value to be 0·0009. The correction factor would be, from this formula, (2·3 − 0·54) 0·0009 = 0·002 and the correction $C \times 0{\cdot}002$ (negative) 0·001°. (Milk was not included in the list of substances examined.)

These values are approximations only, since, in calculating them, several assumptions have been made which, in fact, are not quite correct; they should, however, indicate the order of magnitude of the error in the freezing-point depression due to the difference between the convergence temperature and the observed freezing-point.

In the precise apparatus designed by Raoult and with the technique he adopted, the convergence temperature was only 0·1° above that of the cooling-bath, while the corresponding figure for the 1914 model of Monier-Williams was 0·24°; in the experiments recorded in this paper with the new cryoscope of Monier-Williams, the figure was found to be about 2·1°, suggesting that a much larger amount of heat per unit of weight of liquid gains access to the contents of the freezing-tube. If this is so, it would seem to be a disadvantage, for variations in the temperature of the surrounding air—and such fluctuations are unavoidable—would be expected to have a greater influence on the convergence temperature when the cooling-bath is kept at a constant temperature. The corresponding difference in the Hortvet apparatus amounts to about 0·7°. Thus in Raoult's and Hortvet's instruments it would appear that less heat gains access to the liquid under examination, or, what seems less likely, from a consideration of the apparatus, more heat is abstracted by the cooling-baths.

Raoult[5] (p. 15) specified, when stating the requirements for a satisfactory cryoscope that, first, radiation from the freezing-tube to the cooling-bath should be reduced to a minimum; and secondly, that the heating action of the atmosphere should be eliminated as far as possible. He reduced the heat abstraction from the freezing-tube by the use of an air-jacket about 2·5 mm. in thickness, and took steps to prevent the ingress of heat from the atmosphere. He was, apparently, so successful in carrying out these two objects that he found the difference between the temperature of the cooling-bath and the convergence temperature to be independent of the temperature of the surrounding air and directly proportional to the heat generated by stirring, which is under control and can be kept constant. In the Hortvet and Monier-Williams instruments, on the other hand, the heat caused by stirring is insignificant compared with that leaking in from the surroundings; the temperature of the air will vary from time to time, and the amount of heat entering cannot be regulated; from what has been said above, the variation might be expected to have a greater effect on the convergence temperature with the Monier-Williams cryoscope.

The insulation of the freezing-tube from the heat of the atmosphere is not nearly as efficient in either the Hortvet or the Monier-Williams cryoscope as in Raoult's instrument. Indeed, no special precautions are taken to secure this end. The fact that, of the two, less heat finds access to the freezing-tube in the Hortvet apparatus is probably due to its being composed of glass and being supported in the mouth of the metal tube of the cooling-bath by means of a rubber band, while the Monier-Williams instrument, used in these experiments, has a thin brass freezing-tube and no rubber band is used between it and the metal lining in the hole of the cover of the apparatus. Substitution of a glass tube might result in less heat entering from the atmosphere.

SUMMARY.—The cooling baths of the Hortvet and Monier-Williams cryoscopes are compared as regards their efficiency and convenience in use.

It is concluded that in both designs of instrument there is residual heat transference, that is to say, when no alcohol is present in the jacket surrounding the freezing-tubes, the milk under examination is still subject to an influence depending on the heat abstracted by the cooling-bath maintained at −3·0° and the heat gaining access from the atmosphere and generated by stirring.

The error on this account is greater in the case of the Hortvet apparatus than in the Monier-Williams cryoscope, mainly because the convergence temperature is further from the observed freezing-point.

There are considerable difficulties, from a theoretical point of view at least, in the way of obtaining an accurate measure of the value of the heat-transference factor in both the Hortvet and the Monier-Williams instruments, owing to the fact that when the alcohol is removed from the jacket surrounding the freezing-tube there is residual heat transference; an error due to this cause will affect the supercooling correction. The only procedure, free at any rate from theoretical objections, appears to be so to arrange the conditions of experiment that the convergence temperature coincides with the apparent freezing-point. By this means the heat-transference factor is rendered negligible, and a correct supercooling factor can be ascertained, enabling the true freezing-point to be calculated.

My thanks are due to Mr. G. D. Elsdon for interest and for facilities to carry out the above work.

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LANCASHIRE COUNTY COUNCIL LABORATORY
LIVERPOOL

A Modified Hortvet Apparatus and the True Freezing-point of Milk

BY J. R. STUBBS, M.SC., F.I.C.

(Communicated through the North of England Section)

IN the standard Hortvet process for the determination of the freezing-point of milk, methylated spirit is used in the space surrounding the freezing-tube, in order to facilitate the action of the cooling-bath. When an attempt is made to ascertain the supercooling and heat-transference factors, the removal of this alcohol becomes necessary. In previous papers[1,2] it has been shown that, after this has been done, there is still a nett loss of heat suffered by the freezing-tube and contents when the cooling-bath is maintained at —3·0°, and that, consequently, the values of the two factors are affected.

It was pointed out that the clearance was only about 1 mm. between the freezing-tube and the metal tube of the cooling-bath. This space, on account of its smallness, was not only inconvenient, but could scarcely be expected to serve efficiently as a heat insulator. It was stated that a modification was contemplated in which the clearance would be increased by using a freezing-tube of smaller diameter. Accordingly, a freezing-tube of average external diameter of 27 mm. was used, which left a clearance of 2·5 mm. between it and the metal tube of the cooling-bath. Actual measurements differed very little from the average of 27 mm.

The smaller internal diameter of the freezing-tube necessitated the use of a stirrer with a smaller loop and 30 ml. of liquid only were required to fill the tube to about the same level as 35 ml. in the standard tubes; 60 ml. of methylated spirit were required, in place of about 35 ml. in the standard instrument.

Experiments were carried out to test the efficiency as regards heat insulation of a clearance of 2·5 mm. outside the freezing-tube, as compared with about 1 mm. in the standard apparatus. Mechanical stirring was carried on at the rate of 40 up-and-down strokes per minute. A thick rubber band at the flange of the freezing-tube supported it in the metal tube of the cooling-bath. The freezing-tube was kept central in the metal tube by means of two rubber bands passed round the lower portion and three short lengths of glass rod of uniform diameter held vertically underneath them. The tube so fitted passed into the metal tube of the cooling-bath with practically no play.

The cooling-bath was kept as nearly as possible at —3·0° C. The temperature of the atmosphere was 17° C.

In the first experiment the freezing-tube contained 30 ml. of 15 per cent. alcohol. When the freezing-point thermometer registered about —0·4° the methylated spirit was drawn off, and the experiment carried out with the surfaces of the jacket in a wet state. The temperature fell, by gradually decreasing amounts in a unit of time, to —1·25°, where it remained constant. The convergence temperature, then, under these conditions was —1·25°.

Another experiment was carried out, using 30 ml. of milk, but in all other respects the conditions were the same as previously. The convergence temperature in this case was —1·18°.

With standard Hortvet tubes I found[2] that the convergence temperature was about —2·3°. The effect of increasing the clearance between the freezing-tube and the metal tube of the cooling-bath from approximately 1·0 mm. to 2·5 mm., and using no alcohol in the jacket surrounding the freezing-tube in both cases, is to raise the convergence temperature to about —1·2°. This is a result which would naturally be expected, since the rate of abstraction of heat by the cooling-bath has been diminished by increasing the air space between it and the freezing-tube, and the rate at which heat gains access is not very different in the two instances; that is, the heat insulation between the freezing-tube and the cooling-bath has been made more effective. When the usual amount of super-cooling is employed in an experiment—about 1·2°—the temperature of the milk in the freezing-tube is about —1·7°; the convergence temperature, using the standard

Hortvet tube (—2·3°) is well below this temperature, while with the modified freezing-tube the temperature of convergence (—1·2°) is above it.

It has been shown in a former paper[2] that when the convergence temperature differs from the observed or apparent freezing-point, the effect on the freezing-point is directly proportional to the difference; this statement, according to Raoult,[3] holds good with a high degree of approximation. The correction to be applied to the observed freezing-point depression will be negative whether standard or modified freezing-tubes are used, because in each case the convergence temperature is below the observed freezing-point. This negative correction with the narrower tubes will be diminished by a small positive correction, due to the fact that the convergence temperature is above the point at which supercooling is arrested.

It follows, therefore, that the observed freezing-point will be nearer to the true freezing-point when the modified tubes are employed or, in other words, the heat-transference factor will be less.

It was found[2] that the convergence temperature of the new Monier-Williams cryoscope was about —0·9°. The Hortvet apparatus, modified by the use of narrower tubes, resembles the Monier-Williams apparatus in that the convergence temperature lies between the usual temperature when supercooling is arrested (about —1·7°) and the observed freezing-point; they both differ from the standard Hortvet apparatus where the convergence temperature is below the temperature of the milk at the usual degree of supercooling.

On practical grounds there is little to choose in this particular respect between the new Monier-Williams cryoscope and that of Hortvet fitted with the narrow tubes. If we take the formula given by Raoult[3] for the influence on the freezing-point depression due to the difference between the convergence temperature and the observed freezing-point, *viz.* $C' - C = Cdq$, where C' = observed freezing-point depression; C = true freezing-point depression; d = difference between the convergence temperature and the observed freezing-point, and q a constant which Raoult found to have an average value of 0·0009,* we have: for the Monier-Williams cryoscope $C' - C = C \times (0{\cdot}9 - 0{\cdot}54)\ 0{\cdot}0009 = C \times 0{\cdot}0003$ or 0·00015°, and for the modified Hortvet $C' - C = C \times (1{\cdot}2 - 0{\cdot}54)\ 0{\cdot}0009 = C \times 0{\cdot}0006$ or 0·0003°; these results differ by insignificant amounts.

So much has been said in connection with the application of cryoscopy to milk about the obtaining of "true" freezing-points, that it is desirable to point out that none of the forms of apparatus and technique mentioned in this paper will give absolutely exact values for the supercooling and heat-transference factors when the cooling-bath is maintained at —3·0°, owing to an amount, greater or smaller, of residual heat transference, and therefore to that extent, at least on theoretical grounds, there are objections to calculating "true" freezing-points from the data obtained. It would appear that figures for true freezing-points which shall be free from such theoretical objections necessitate the use of much more complicated apparatus and technique.

Raoult and Monier-Williams each endeavoured to design such an instrument, and just before freezing was induced adjusted the temperature of the cooling-bath, so that the convergence temperature was identical with the observed freezing-point. At the apparent freezing-point the contents of the freezing-tube were in thermal equilibrium with their surroundings, and the cooling-bath had no effect on the freezing-point; the influence of the small amount of heat transference during the rising of the temperature from the lowest to the highest point on freezing was regarded as negligible.

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* This factor was not found for milk, and might be expected to vary somewhat with different types of apparatus.

If it be objected that the modified Hortvet freezing-tubes described in this paper are unsatisfactory because they involve the use of a smaller quantity of milk, 30 ml. as compared with 35 ml. in the standard Hortvet process, the standard Hortvet tubes might be used, and the metal tube of the cooling-bath replaced by one 5 mm. greater in internal diameter; this modification would entail the use of a smaller quantity of ether in the cooling-bath.

SUMMARY.—A modification of the standard Hortvet apparatus is described, consisting in the use of freezing-tubes of such dimensions as to allow a clearance of 2·5 mm. between these tubes and the metal tube of the cooling-bath. The results so obtained when the cooling-bath is maintained at −3·0° and alcohol is removed will not be very seriously influenced by residual heat transference, resembling, in this respect, those given by the new Monier-Williams cryoscope.

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LANCASHIRE COUNTY COUNCIL LABORATORY
LIVERPOOL

Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF ELEMENTAL SULPHUR

FLECK and Ward (ANALYST, 1934, 59, 636) have recently described a method for the determination of elemental sulphur in which they heat a weighed quantity of the material, containing about 0·1 g. of sulphur, with 2 g. of crystalline sodium sulphite and 30 to 40 ml. of water in a conical flask attached to a reflux condenser. The sulphite and sulphur combine to form thiosulphate, which is titrated with iodine, after any remaining sulphite has been inactivated with formalin and acetic acid. We have tried this method on several samples of sulphur ointment, but find that it gives low results compared with the method of direct oxidation to sulphuric acid by bromine and nitric acid, described by Evers and Elsdon (*Analysis of Drugs and Chemicals*, p. 260).

With certain samples of ointment it was impossible to obtain anything like complete solution with 2 g. of sodium sulphite, and twice this amount was found to be necessary. Even so, the results were still low, as is shown by the following figures:

	Evers and Elsdon Per Cent.	Fleck and Ward Per Cent.
Sample 1	11·2	10·2
,, 2	10·7	10·2
,, 3	10·7	10·0
,, 4	10·5	10·1
,, 5	10·3	9·8
,, 6	10·3	9·2
,, 7	10·1	8·1

Careful examination of the condenser showed that some of the sulphur was volatilised into it, and could be effectively removed therefrom only by washing with carbon disulphide.

A further disadvantage of the method, from the point of view of the Public Analyst, is that, on keeping, some of the sulphur may enter into combination with the ointment base. The Pharmacopoeia requires that 10 per cent. of sulphur be employed in the compounding of the ointment, and the analyst is therefore called upon to determine the full amount of sulphur present in the ointment and not that which may still remain in the elemental condition.

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ANALYSIS OF MEAT AND BONE MEALS

The note by Sherratt (Analyst, 1935, 170) on discrepancies in the analyses of meat and bone meals might lead one to infer that these are due exclusively to the retention of combined moisture in the bone. Although we do not analyse many bone meals as low in fat and protein as that cited in the note, yet with the average meat and bone meal obtained exclusively from fresh freezing works bye-products, containing from 10 to 30 per cent. of ash, we doubt whether the discrepancy is due to combined water. Such meals usually contain a small quantity of vegetable matter which has escaped removal during the washing of the raw material. Apart from this and the presence of small quantities of glycogen, the discrepancy is due mainly to the arbitrary protein factor (6·25) not being in accord with the nitrogen-content of the protein present in the meal. It is, of course, recognised that, on the average, this factor should be a little higher, but there is an additional factor to contend with, in that the nitrogen-content of protein from this source is variable and depends to some extent on the age of the animals being slaughtered. The discrepancy is greater in meals made during periods when the raw material is derived almost wholly from lambs or during the season when "bobby calves" are being killed, and there is strong evidence that the nitrogen-content of protein from immature animals is lower than in that from mature animals.

In order to overcome this difficulty of discrepancy in the analysis of meat meals, this laboratory, many years ago, adopted the policy of describing the difference as "organic matter other than fat and protein." It is realised, of course, that there are many objections to this description, but it seemed undesirable to depart from the universal factor for calculating nitrogen to protein in feeding meal generally. At the same time the difference could not be described as wholly due to carbohydrates.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND COUNTY OF BRISTOL

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1934

OF the 1384 samples of food and drugs examined, 691 were taken formally.

"SPIRIT OF IODINE."—There is a large sale of solution of iodine by pedlars in the streets of Bristol. One sample was condemned as being deficient in iodine to the extent of 79·1 per cent., and in potassium iodide to the extent of 65·5 per cent. Another sample, which was called "spirit of iodine," had the following composition: Iodine, 0·8 g.; potassium iodide, 1·25 g.; phenol, 2 g.; and industrial spirit and water to produce 100 ml. There is no such preparation as "spirit of iodine" in the B.P. or B.P. Codex, and it is conceivable that the article might be purchased for the tincture or solution of iodine.

LEAD IN SARDINES.—Five port samples of sardines contained 8, 5, 5, 1·5, and 0·3 parts per million of lead, respectively. This is well below the limit of 20 p.p.m., suggested at the conference of port medical officers held at the Ministry of Health on October 20, 1933.

FORMIC ACID IN SUGAR.—A port sample of soft cane sugar contained 0·10 per cent. of formic acid preservative.

F. E. NEEDS

COUNTY OF DERBY

ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1934

OF the 2026 samples examined under the Food and Drugs (Adulteration) Act, 412 were taken informally.

ADULTERATION OF MINT WITH AILANTHUS.—Four of nine samples of dried mint were adulterated with *Ailanthus glandulosa.* This adulteration, which was detected some years ago (*cf.* ANALYST, 1934, **59**, 33), appears to be carried on still. One sample was stated to be a recent delivery from the wholesale dealers, and proceedings were instituted. Having regard to the fact that all deliveries made by the wholesale firm had been recalled, the magistrates found the vendor guilty of a technical offence and dismissed the case on payment of £1 15s. 6d. costs.

R. W. SUTTON

CITY OF PORTSMOUTH

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1934

THE total number of samples of food and drugs examined was 1253, corresponding with a sample rate of 4·9 per 1000 of population.

ICE-CREAM.—Thirteen samples, taken during the months of June and July, were representative of the article sold in shops and from carriers on cycles. The chemical and bacteriological results were as follows:

Sample No.	Total solids Per Cent.	Fat Per Cent.	Mineral matter Per Cent.	Starch	Bacteria on agar in 1 ml.	*Bacillus coli* Test
1	35·0	14·3	0·6	Absent	800,000	Positive for 1/1000th ml.
2	38·7	13·4	0·8	Absent	29,100	Positive for 1/10th ml.
3	34·2	10·8	1·1	Absent	122,400	Positive for 1/1000th ml.
4	35·6	8·0	1·1	Absent	4,900	Absent from 1 ml.
5	39·7	12·0	0·8	Absent	310,500	Positive for 1/100th ml.
6	35·0	14·3	0·6	Absent	42,000	Positive for 1/1000th ml.
7	35·0	14·3	0·6	Absent	310,000	Positive for 1/1000th ml.
8	24·3	3·6	0·7	Present	113,000	Positive for 1/1000th ml.
9	30·3	13·1	0·5	Present	160,000	Positive for 1/1000th ml.
10	26·9	2·8	0·6	Present	40,000	Positive for 1/1000th ml.
11	26·7	4·0	0·6	Present	432,000	Positive for 1/1000th ml.
12	24·0	1·4	0·3	Present	Uncountable	Positive for 1/1000th ml.
13	28·2	2·9	0·5	Present	156,000	Positive for 1/1000th ml.

Samples Nos. 1 to 7 are typical of the better kind of ice-cream, which is made from milk or milk powder, sugar and butter or cream, with a small proportion of gelatin. These materials form the "mix," which should be pasteurised before being frozen. The other kind of ice-cream is made by heating milk with cornflour, which is then suitably flavoured, coloured and frozen. Samples Nos. 8 to 13 are of this type.

If these samples are judged by the Standard for Grade A milk, it will be seen that Nos. 1, 5, 7, and 11 have an excessive number of bacteria, and that only Nos. 2 and 4 would pass the *B. coli* test. This position is unsatisfactory, but it is not likely to be materially improved until the "mix" is pasteurised and all utensils used in the preparation of ice-cream are sterilised. R. P. PAGE

Department of Scientific and Industrial Research

REPORT OF THE CHEMISTRY RESEARCH BOARD*

THE report provides the first complete survey of the work carried out in the Chemical Research Laboratory during the ten years of its existence. It opens with a historical introduction by the Director of Chemical Research (Professor G. T. Morgan), in which are given an account of the origin of the Chemical Research Laboratory and of its administration and control, a survey of the early years of the laboratory, and an outline of its associations with chemical industry. Several firms have made arrangements for members of their staffs to become acquainted with the new methods and technique developed there.

At the present time the scientific and technical staffs, who, for administrative purposes are grouped in ten sections, are occupied in some twelve specific items of research, and, in addition, a certain amount of general research is carried out at the discretion of the Director.

In the Report there is an explanatory section preceding the report of each section's work during the past year.

CORROSION OF METALS.—In general, the work aims at the investigation of the mechanism of corrosion in its relation to the prevention of rusting, tarnishing and the corrosion of metals in industrial use.

Special techniques have been developed for following the progress of corrosion over long periods of time. With metals totally immersed in salt solutions, provision has been made for measurements under high oxygen pressures and for distinguishing between corrosion corresponding with hydrogen evolution and with oxygen absorption. For metals exposed to dry or humid atmospheres the methods used are sensitive to very small amounts of attack. Corrosion of the following metals has been investigated: zinc, highly-purified iron, carbon sheets, magnesium and some of its light alloys, copper and nickel.

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* Report for the period ended December 31st, 1934. H.M. Stationery Office. Pp. v + 94. Price 1s. 6d. net.

The anodic oxidation process, in which aluminium is protected from corrosion by an oxide film produced electrolytically, was worked out under the Department, and this work has led to the discovery of a means for the colouring of aluminium, which is now being taken up actively by the industry.

Other problems dealt with have been the corrosion of locomotive boiler tubes and the rapid production of the green patina on copper sought after by architects and sculptors.

HIGH PRESSURE RESEARCH.—Alcohols, including ethyl alcohol, have been produced by direct interaction of carbon monoxide and hydrogen under pressure, and acetic acid has been obtained by the interaction of ethyl alcohol and carbon dioxide. Equipment has recently been constructed for work at a pressure of 3000 atmos. at 200° C.

Helium from Monazite Sand.—In the manufacture of incandescence gas mantles from monazite sand the helium is lost. A process whereby helium of 99·6 per cent. purity is obtained has been worked out, the sand being heated in an atmosphere of carbon dioxide.

Preparation of Carbon Monoxide.—The carbon monoxide used in high-pressure experiments was made from formic and sulphuric acids. Gas of 99·5 per cent. purity is also supplied by the Chemical Research Laboratory to outside firms and research institutions.

COAL TAR.—By means of a new method of separation the Chemical Research Laboratory has been able to identify and classify many of the numerous components contained in tars produced by different methods. During the course of this work it was found that certain tars contained constituents of a phenolic nature, which could be readily separated by distillation. Dissolved in caustic soda solution, these have been found to form a very efficient and cheap wetting-out agent for use in the textile industry. The material is now being sold under the name of "Shirlacrol." Samples have been supplied to 21 firms, and uniformly good reports of its effects have been received.

As the result of the application of high pressure technique to coal tars, new compounds have been formed and have been tested for their possible use in the dye industry.

SYNTHETIC RESINS.—As a result of experiments in the Chemical Research Laboratory, a tough, transparent resin, resembling glass, has been obtained, and this may also find application as a material for artificial dentures. In connection with this work, it is interesting to note that, with the object of making synthetic resins direct from tar oils, experiments in progress indicate the possibility of simultaneously separating the valuable hydrocarbon oils. Resins formed in this way have been favourably reported on for impregnation purposes, as they serve to prevent the growth of mildew.

ROAD TAR.—Since 1931 work has been proceeding at the Chemical Research Laboratory, in co-operation with the British Road Tar Association, on researches for the improvement of the quality and efficiency of road tars. One interesting result obtained is that light, in addition to air, may be of great importance in connection with the life of the tar that is applied to roads.

TREATMENT OF ROPES AND CORDAGE.—The decay of ropes and fibres through attack by micro-organisms has been shown to depend on moisture conditions.

In 1932-33, for example, it was found that ropes were more likely to be attacked when stored near the Thames estuary than when stored on the south-west coast. Coils of rope are now impregnated with a copper salt which prevents microbiological decay.

Degumming of Silk.—As a result of tests conducted with over 160 species of lower fungi, it has been found that *Aspergillus niger* is capable of degumming silk more rapidly and thoroughly than the acids usually used.

Earthy Taste in Salmon.—Another instance of the application of microbiology is afforded by a recent investigation on the cause of earthy taste in salmon taken from a well-known salmon river. Investigation on the spot proved that the earthy taste and odour were due to the tainting of the river by growths of certain organisms (*e.g.* a type of *Actinomyces*). It was found that the taint disappeared if the fish were kept for two to five days in clear running water. Investigations are proceeding to determine the composition of the material responsible for the tainting of the fish.

DRUGS.—The Chemistry Research Board have arranged for the preparation of synthetic chemicals of the types likely to be useful in the treatment of disease, and, by co-operation with the Medical Research Council, to have them tested for their chemotherapeutical effects. This arrangement covers not only chemicals that are produced in the Chemical Research Laboratory, but also those produced by workers in Universities who are assisting in this branch of the work.

OTHER INVESTIGATIONS.—The report also refers to investigations which are being carried out on behalf of the Department's Water Pollution Research Board. It is now possible to prepare from British clays base-exchange materials for water-softening which are superior to some of the treated natural materials at present imported. Work is also being undertaken on the action of water on lead, and a summary of the existing knowledge of the action of drinking water on lead has recently been published (ANALYST, **1934**, **59**, 346).

One of the features of modern industry, the report states, is the increasing use which is made of the rarer metals. Accordingly the extraction of these metals from British minerals is under investigation, and their compounds are being prepared. Some of them have been used in connection with fundamental work on the co-ordination theory of valency and chemical constitution.

All-India Institute of Hygiene and Public Health

ANNUAL REPORT FOR THE YEAR 1934

THIS is the first Annual Report of the Institute, which was formally opened in December, 1932, in Calcutta. The scientific control of the Institute is vested in a committee which includes (i) the Member of the Governor-General's Executive Committee in charge of the Department of Education, Health and Lands, or the Secretary of the Department (President); (ii) the Director-General, Indian Medical Service; (iii) the Public Health Commissioner with the Government of India; (iv) the Director, School of Tropical Medicine, Calcutta; (v) the Director, All-India Institute of Hygiene and Public Health; (vi) one medical or scientific non-official member of the Governing Body of the Indian Research Fund Association; (vii) one medical non-official member of the Governing Body of the India Research Fund Association; (viii) a representative of the Legislature.

The Institute, which is under the direction of Lt.-Col. A. D. Stewart, M.B., F.R.C.S.E., D.P.H., has six sections:—(i) Public Health Administration; (ii)

Malariology and Rural Hygiene; (iii) Epidemiology and Vital Statistics; (iv) Nutrition and Biochemistry; (v) Sanitary Engineering; (vi) Maternity and Child Welfare. Reports of the directors of each of the sections are given.

In the Report of the Professor of Biochemistry and Nutrition (Dr. H. E. C. Wilson) it is stated that the policy has been to make as complete analyses as possible of Indian foodstuffs. In the course of this work special investigations have also been undertaken.

VITAMIN *C* CONTENT OF INDIAN FOODSTUFFS.—It has been found that titration with 2:6-dichloro-phenolindophenol affords accurate results, provided that the titration is carried out within one minute. Among the fruits rich in vitamin *C* are papaya, pineapple, leechee and guava, whilst fruits and vegetables poor in vitamin *C* are onions, bananas, apples, melons, pears, peaches, plums, and grapes. Vegetables such as cabbage, radish leaves, karela, certain varieties of red pepper and spinach are all rich in this vitamin, in contrast with the cauliflower, pumpkin, and allied species. The effect of moderate cooking is to reduce the vitamin-content by 20 to 25 per cent.

RADIO-ACTIVE WATER AND VITAMIN DEFICIENCY.—Work on the effect of radio-active waters on the symptoms of vitamin deficiency in rats tends to indicate that such waters may prevent and cure the early symptoms of vitamin deficiency, such as xerophthalmia. The duration of life also appears to be prolonged.

PREPARATION OF VITAMIN *B* CONCENTRATES.—Work has been done on the preparation of pure vitamin concentrates of the *B* group from various sources. Concentrates of B_1 (antineuritic), of B_2, and of a fluorescent flavine pigment with B_2 properties have been obtained. The investigation of the problem of the symptoms of deficiency of vitamin B_2 may be materially forwarded by the photometric estimation of minute quantities of the fluorescent pigment in foods and tissues.

Commonwealth of Australia

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

Division of Forest Products*

No. 16. IDENTIFICATION OF THE PRINCIPAL COMMERCIAL AUSTRALIAN TIMBERS OTHER THAN *EUCALYPTS*

A KEY for the identification of the Australian *Eucalypts* has already been published (ANALYST, 1935, **60**, 475), and in the present key special attention is devoted to features that might lead to confusion between the *Eucalypts* and the other woods. The key is based principally on macroscopic features as follows:

GENERAL PROPERTIES.—Colour, odour, weight, grain, fissility, texture, hardness, burning splinter test (*loc. cit.*). Photographs (10 to 35×) illustrating details of structure revealed by the hand-lens were prepared after rubbing-down the specimen with water on a slate and polishing with a tooth-brush.

PORES.—The samples are first divided into pored woods (hardwoods) and non-pored (soft or coniferous) woods, the majority of the commercial Australian timbers being in the former class.

(*a*) *Number of Pores.*—A circular metal die (area 20 square mm.) is impressed on the cross-section of the wood in a number of places, and the number of pores in each circle is counted and an average taken.

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* Technical Paper No. 16, 1935, pp. 103 + 56 plates. By H. E. Dadswell and A. M. Eckersley. No. 23, *J. Council Sci. and Indust. Res.*, 1935, **8**, 27–36, by W. E. Cohen.

(*b*) *Size of Pores.*—Four classes are recorded, *viz.* below 100 microns (very fine texture), 100 to 200, 200 to 300, and over 300 microns (coarse).

(*c*) *Arrangement of Pores.*—Solitary or pairs and trios (or both), long chains, and clusters.

VESSELS, LINES AND CONTENTS are observed with a lens on freshly-split radial surfaces, and are classified as simple or scalariform. The presence of tyloses and extraneous material is recorded.

PARENCHYMA.—Woods (examined in cross-section) are classified in terms of this characteristic as follows:

(*a*) *Paratracheal, i.e.* gathered about the vessels in vasicentric, aliform or confluent patterns.

(*b*) *Metatracheal, i.e.* in concentric bands more or less parallel to the growth-bands, and independent of the pores.

(*c*) *Diffuse, i.e.* scattered irregularly. Crystals may often be detected in the parenchyma if the wood is wetted.

RAYS.—The size and number in a cross-section are recorded. Rays may be homogeneous (when all the component cells are radially elongated), or heterogeneous (when the cells differ in size and shape).

GUM DUCTS may be vertical or horizontal.

RIPPLE MARKS are fine horizontal lines or bands which are visible under the lens on the tangential surfaces of certain timbers.

MINUTE ANATOMY.—The full results of the microscopical examination of the sections of the woods are not recorded, but sufficient information is given on special features to assist identification.

Descriptive notes on the above lines are given for each of the timbers examined, together with reasons for the particular value of the species, and means of separation from timbers of similar appearance and structure. In addition to the full key of identification, the timbers are also listed under their various distinctive anatomical features as follows:

(*a*) **Timbers possessing a Characteristic and Distinctive Odour.**—*Doryphora sassafras, Daphnandra micrantha* (faint), *Cryptocarya erythroxylon, Endiandra palmerstoni, Ceratopetalum apetalum, Acacia acuminata, Acacia cambagei, Cedrela toona* var. *australis, Dysoxylon fraseranum, Ehretia acuminata* (faint), Genus *Callitris, Dacrydium franklinii.*

(*b*) **Timbers definitely Ring-porous.**—*Cedrela toona* var. *australis, Melia azedarach* var. *australasica, Ehretia acuminata.*

(*c*) **Timbers showing "Ripple Marks" (Macroscopic).**—*Albizzia toona* (some samples), *A. xanthoxylon, Castanospermum australe, Brachychiton acerifolius, Tarrietia actinophylla, T. argyrodendron, T. argyrodendron* var. *peralata, Olearia argophylla* (faint).

(*d*) **Vessels Absent.**—*Agathis palmerstoni, A. robusta, Araucaria cunninghamii, A. bidwilli, Athrotaxis selaginoides, Callitris glauca, Pinus radiata, Dacrydium franklinii, Phyllocladus rhomboidalis, Podocarpus elata.*

(*e*) **Intercellular Canals in Pored Timbers.**—(i) Vertical.—*Flindersia australis, F. brayleyana, F. pubescens, Cedrela toona* var. *australis.*

(ii) Horizontal.—*Protium australasicum, Euroschinus falcatus, Pleiogynium solandri, Rhodosphaera rhodanthema, Tieghemopanax elegans, Alstonia scholaris.*

(*f*) **Resin Ducts (Non-pored Timbers).**—*Pinus radiata* and others of genus *Pinus.*

(*g*) **Solitary Pores.**—*Casuarina* spp., *Villaresia moorei, Calophyllum costatum, Melaleuca* spp., *Syncarpia laurifolia, S. hillii, Tristania conferta, T. suaveolens, Symplocos spicata.*

(*h*) **Pores in Rows or Groups Forming with Confluent Parenchyma Tangential Loops between Rays.**—*Banksia* spp., *Cardwellia sublimis, Embothrium wickhami, Grevillea robusta, G. striata, Orites excelsa.*

(*k*) **Pores in Long Radial Chains.**—*Geissois benthami, Schizomeria ovata, Weinmannia lachnocarpa, Albizzia toona, A. xanthoxylon, Castanospermum australe, Acradenia frankliniae, Flindersia ifflaiana, Flindersia oxleyana* (?), *Phebalium squameus, Lucuma galactoxyla, S. australe. S. pohlmanianum, S. richardi.*

(*l*) **Pores in Oblique Chains.**—*Acradenia frankliniae, Phebalium squameus, Calophyllum costatum.*

(*m*) **Vessel Element Perforation Plates Scalariform.**—*Atherosperma moschatum, Daphnandra micrantha, Doryphora sassafras, Ackama muelleri, Villaresia moorei, Eucryphia billardieri, Symplocos spicata.*

(*n*) **Vessel Elements with Scalariform Pitting** (Microscopic Feature).—*Atherosperma moschatum* (?), *Daphnandra micrantha* (?), *Doryphora sassafras, Ackama muelleri, Anodopetalum biglandulosum, Ceratopetalum apetalum, C. virchowii, Eucryphia billardieri.*

(*o*) **Vessel Elements with Spiral Thickenings** (Microscopic Features).—*Nothofagus moorei, Acradenia frankliniae, Ehretia acuminata.*

(*p*) **Parenchyma Definitely Aliform and/or Confluent.**—*Banksia* spp., *Cardwellia sublimis, Embothrium wickhami, Grevillea robusta, G. striata, Orites excelsa, Albizzia toona, A. xanthoxylon, Castanospermum australe, Angophora* spp., *Eugenia* spp., *Harpullia pendula.*

(*q*) **Parenchyma in Metatracheal Bands.**—*Aphananthe philippinensis, Ficus macrophylla, Pseudomorus brunoniana, Beilschmiedia obtusifolia, Cryptocarya erythroxylon, C. oblata, Endiandra palmerstoni, Ceratopetalum apetalum, C. virchowii, Acradenia frankliniae, Flindersia australis, F. ifflaiana, F. pubescens, F. schottiana, Halfordia drupifera, Dysoxylon fraseranum, D. muelleri, Sloanea woollsii, Brachychiton acerifolius, Tarrietia actinophylla, T. argyrodendron, Calophyllum costatum.*

(*r*) **Parenchyma in Fine Metatracheal Rows between Rays.**—*Casuarina* spp., *Schizomeria ovata, Geissois benthami, Weinmannia lachnocarpa, Aleurites moluccana, Villaresia moorei, Lucuma galactoxyla, Sideroxylon australe, S. pohlmanianum, S. richardi, Symplocos spicata, Alstonia scholaris, Ehretia acuminata.*

(*s*) **Oil Cells in Vertical and Ray Parenchyma.**—*Beilschmiedia obtusifolia, Cryptocarya erythroxylon, C. oblata, Litsea reticulata, Endiandra palmerstoni.*

(*t*) **Broad Rays.**—*Casuarina* spp. (except *C. lepidophloia*), *Banksia* spp., *Cardwellia sublimis, Embothrium wickhami, Grevillea robusta, G. striata, Orites excelsa.*

(*u*) **Timbers with two types of Rays.**—(i) **Fairly large and Broad.** (ii) **Very Fine but More Numerous.**—*Villaresia moorei, Elaeocarpus grandis, E. obovatus, Sloanea australis, S. woolsii, Brachychiton acerifolius, Tarrietia actinophylla, T. argyrodendron,* var. *peralata, Symplocos spicata.*

(*v*) **Septate Fibres.**—*Litsea reticulata, Protium australasicum, Dysoxylon fraseranum, D. muelleri, Euroschinus falcatus, Pleiogynium solandri, Rhodosphaera rhodanthema, Gmelina leichhardtii, Vitex lignum-vitae.*

No. 23. A CHEMICAL INVESTIGATION OF *PINUS RADIATA* IN RELATION TO ITS PAPER-MAKING QUALITIES. Part I. THE DISTRIBUTION AND NATURE OF THE NON-VOLATILE ETHER EXTRACTIVES

As a result of afforestation schemes in Australia and New Zealand, large areas of pines, mainly *Pinus radiata* (*insignis*), are now available. For economic reasons it is undesirable to convert these into pulp for paper by means of the usual alkali processes, and acid processes produce (probably as a result of polymerisation) resinous matters similar to pitch, which are objectionable. Early work on the subject indicated that green sapwood gives no trouble in this respect, and that the resins naturally present in heartwood give trouble only when modified by the cooking process. There should, therefore, be an increase in the amount of material soluble in ether, and a change in its chemical nature, during the transition from sapwood to heartwood; this transition does not usually commence before the tree is 20 years old.

In the present work 85 samples of wood from S. Australia, Victoria and New Zealand, 6 to 22 years old, were extracted with dry ether, free from acidity, the extract being evaporated, and the residue dried at 55° to 60° C. The acid value was determined by titration of an alcoholic solution with 0·5 N potassium hydroxide solution in the presence of phenolphthalein, and the ester value by subsequent removal of the alcohol by evaporation and saponification of the resulting residue; experimental sulphite pulping tests were also made.

The results show that there is no definite relationship between the yield of extractives from a whole log section and the age of the tree or the amount of heartwood present, and that it is desirable to take into account seasonal variations and changes in the nature and quantity of the material soluble in ether during storage. The pulping tests confirmed the fact that pine wood containing appreciable amounts of heartwood is difficult to pulp and occasions "pitch" trouble; pulp from sapwood and heartwood contained 0·35 and 3·84 per cent. of extractive, respectively. In all cases the amount of ether-soluble matter was greater in the inner rings than in the outer rings of the log sections, the difference being greatest in the few cases where the former contained much heartwood. The nature of the resin (as indicated by the acid/ester ratio) in the inner rings differs from that in the outer rings only when heartwood is present, formation of the heartwood being accompanied by an increase in acid-content. High yields of extractives having a high ester value are obtained in the presence of bands of resin ducts, and these usually occur in trees 16 to 18 years old. The extractives from younger samples (6 to 12 years old) collected in March had a low acid/ester ratio compared with those collected in September.

J. G.

British Guiana

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1934

In his Annual Report the Government Analyst (Mr. Kenneth Wallis, B.Sc., A.I.C.) states that 6738 samples were analysed, compared with 6462 in 1933 (ANALYST, 1934, **59**, 627).

MILK.—The standard for fat in milk in British Guiana is 3·25 per cent. Of 3848 samples examined, 3634 were genuine. Samples of milk were tested for dirt and extraneous matter by means of the Tankard apparatus, but none was reported against.

COCONUT OIL.—One hundred samples of local coconut oil were analysed under the Copra Ordinance No. 31 of 1933, but, although many samples were reported against, very few convictions were obtained, owing to defects in the Ordinance. Twenty-three samples were condemned as having an acidity (as lauric acid) above 0·15 per cent., and one was a mixture of coconut and soya bean oil.

ILLICIT SPIRIT.—The Police Department submitted 124 samples of spirits to be examined for the presence of illicit spirit (bush rum). Research work on the methods of detection has been continued, and it is now possible to express an opinion on as small a quantity as half a fluid ounce.

AERATED WATERS.—The Department is responsible for the registration and control of the local aerated water factories, and these are frequently inspected with a view to seeing that they comply with the conditions for operating laid down by the Governor in Council. There are at the present time on the register thirty-two of these factories widely distributed in the Colony. The use of saccharin in sweetened aerated waters is prohibited, and although numerous samples were taken, no saccharin was found during the year. The general standard of cleanliness has greatly improved as a result of the increased number of visits of inspection.

United States Pharmacopoeia Revision*

THE U.S.P.X. Interim Revision Announcement No. 4 includes Magnesia Magma, Oil of Lemon, Non-destearinated Cod-liver Oil, and large and small Tablets of Mercury Bichloride.

Magnesia Magma is described as an aqueous suspension of magnesium hydroxide, containing not less than 7 per cent. and not more than 8·5 per cent. of $Mg(OH)_2$. For flavouring purposes, 0·5 ml. of a volatile oil or blends of volatile oils, per 1000 ml. is suggested, and in order to minimise the action of the preparation on the glass container, 0·1 per cent. of citric acid may be added. It is recommended that storage should be at temperatures not exceeding 35° C., but freezing should not be permitted.

Oil of lemon is described as the volatile oil obtained by expression, without the aid of heat, from the fresh fruit of *Citrus medica* var. *Limonum*, with or without the previous separation of the pulp and the peel. The standards are, sp.gr. 0·849 to 0·855 at 25° C., $[\alpha]^{25}_{D}$ $+57°$ to $+65{\cdot}6°$, and n^{20}_{D}, 1·4742 to 1·4755.

Non-destearinated Cod-liver oil, which is the raw material from which medicinal oil is prepared, is the entire fixed oil obtained from the fresh livers of *Gadus morrhua* Linn. and other species of *Gadidae*, containing nor more than 0·5 per cent. by volume of water and liver tissue, when determined by the method for the determination of water and sediment (Chum) in fatty oils. It contains at least 600 U.S.P. units of vitamin *A*, and at least 85 U.S.P. units of vitamin *D* per g. It is described as a thin oily liquid at normal room temperatures, having a peculiar, slightly fishy, but not a rancid odour, and a fishy taste. It may be stored in a vacuum or in the presence of an inert gas, and should be kept in well-closed containers in a cool place.

Mercuric chloride tablets.—The tablets must be of a distinctive colour (not white), and of an angular or irregular shape (not discoid). When sold in quantities for household use they must be dispensed in glass containers of a distinctive angular shape, having irregular or roughened sides or edges. On each container must be placed a red printed label bearing the word "Poison," and a statement indicating the amount of mercuric chloride per tablet. The large tablets must contain not less than 0·459 g. or more than 0·559 g. of $HgCl_2$ and a sufficient quantity of a suitable excipient or diluent, and the small tablets must contain not less than 0·1125 g. and not more than 0·1375 g. of $HgCl_2$.

S. G. S.

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* *Pharm. J.*, 1935, **134**, 748.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Behaviour of Citric Acid in Boiled Milk. B. Rogina. (*Z. Unters. Lebensm.*, 1935, **69**, 337–340.)—It was stated as early as 1904 (Obermaier, *Arch. Hyg.*, 1904) that the amount of citric acid in milk is considerably decreased on boiling. Obermaier's method consisted essentially in curdling the milk with sulphuric acid, clarifying with "Spanish clay," separating the citric acid from the serum in the form of ammonium citrate and determining it by an oxidimetric method. This procedure is criticised partly on the ground of its complexity and partly on the ground of the introduction of calcium from the earthy material used in the clarification and the consequent precipitation of calcium citrate with the curd.

The author has investigated the behaviour of citric acid in boiled milk by the following method:—The milk (100 ml.) is diluted to about 200 ml., curdled by the addition, drop by drop, of 2 *N* sulphuric acid, made up to 250 ml., and filtered. To 40 ml. of the filtrate, 20 g. of sodium sulphate, 5 g. of sodium nitrate and 20 ml. of Denigès mercury reagent (*cf.* ANALYST, 1898, 23, 161) are added. The mixture is heated to boiling and filtered, and the precipitate is thoroughly washed. To the filtrate and washings, diluted to about 400 ml., 3 or 4 g. of manganese sulphate are added. The gently boiling liquid is then treated with saturated potassium persulphate solution, drop by drop, until all the citric acid is precipitated as the ketonic acid. The supernatant liquid is tested for complete precipitation by the addition of more potassium persulphate. Under these conditions the stated amount of Denigès reagent suffices for the determination of 0·01 to 0·07 g. of citric acid. The precipitate is collected in a Gooch crucible, washed with hot water until free from sulphuric acid, and dried at 105° C. to constant weight. The factor for conversion into citric acid is 0·1764. The method of preparation of the serum by the use of sulphuric acid was found to be the most satisfactory, though coagulation by means of acetic acid was also successfully employed. The use of calcium nitrate (substituted for the more usual calcium chloride to avoid the introduction of chlorions which interfere with the action of Denigès reagent) in the preparation of the serum gave low results, probably owing to the precipitation of calcium citrate. The method was applied to the determination of citric acid in raw milk, before and after heating for 15 minutes over a flame, the water lost by evaporation being determined and replaced. The results obtained indicate that there is no loss of citric acid when the milk is heated to boiling-point, or even when the heating is continued for 15 minutes. A. O. J.

Wheat-rye Flour and Bread. P. Nottin and A. Daron. (*Ann. Falsif.*, 1935, **28**, 281–285.)—Analyses were made of wheat-rye flours containing 85, 50, and 25 per cent. of rye-flour, and baking tests were made with each. The loaves rise less than those made from wheaten flour alone and are less nutritious, owing to the diminished content of nitrogenous matters. When as much as 50 per cent.

of rye-flour is used, the bread keeps fresh much longer than wheaten bread, but the mechanical behaviour of the flour then renders panification troublesome.

T. H. P.

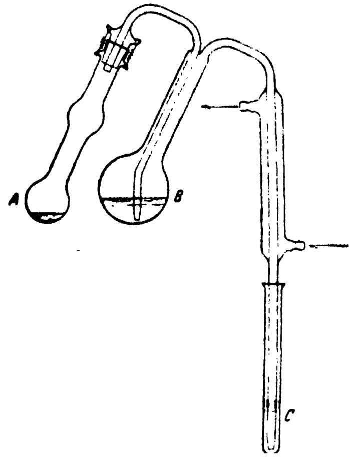
Occurrence of Betaine in Wheat Bran. F. E. Nottbohm and Mayer. (*Z. Unters. Lebensm.*, 1935, **69**, 289–300.)—A determination of the choline-content of bran and conversion of the figure obtained into phosphatide gave values which appeared incorrect and led to the suspicion that another base was present. This base was identified as betaine. It was prepared from bran by extraction of 1 kg. with a mixture of alcohol and benzene. After removal of the solvents the residue was hydrolysed in an autoclave, cleared with animal charcoal, and the base (0·35 per cent.) was separated by precipitation with Dragendorff's reagent. The hydrochloride, unlike choline hydrochloride, is insoluble in cold alcohol, but is soluble in a large volume of boiling 96 per cent. alcohol, from which it crystallises in white glistening plates, m.p. 226° C. The picrate melts at 183·5° C. The hypothesis that wheat flour contains a complex betaine (trigonelline) has been proved incorrect in a previous investigation (*Z. Unters. Lebensm.*, 1934, **67**, 369). Schultze and Pfenniger (*Z. physiol. Chem.*, 1913, **86**, 153) have detected betaine in certain leguminosae and in oats; its presence in the latter is confirmed in this investigation. Experiments, described in detail, have shown that the betaine in bran is not present as a structural component of the phosphatin, but is probably associated with sugar as a complex amino-sugar. A. O. J.

Iodine-content of Georgia Vegetables, and Water as a Factor in its Variation. K. T. Holley, T. A. Pickett and W. L. Brown. (*Bull.* 190, *Georgia Experiment Station, May*, 1935.)—Simple goitre is rare in Georgia, but 109 samples of potatoes showed very low iodine-contents, which averaged 0·054 p.p.m. (on dry matter) and varied little in samples from soils of different types. Moderately high iodine-contents were found in turnip tops (0·226), lettuce (0·363), collards (0·074), pimentos (0·022) and, especially, spinach (0·567). With at least three of these the proportion of iodine tends to increase with increasing water-supply to the growing crop, and the evidence indicates that the water factor alone may account for wide variations in the iodine-content of crops grown under conditions otherwise similar. For the determination of the iodine, the samples were subjected to the low-temperature ashing process (McLendon and Remington, ANALYST, 1929, **54**, 239), which gives somewhat low results. Slight moistening of the material after the preliminary charring and before heating in the muffle (at 435° to 475° C.) considerably reduces the carbon-content of the ash.

T. H. P.

Pigments of Pink Grapefruits, Citrus Grandis (L., Osbeck). M. B. Matlack. (*J. Biol. Chem.*, 1935, **110**, 249–253.)—The pigments occurring in the flesh of pink grapefruits have been extracted with carbon disulphide, and, after purification by treatment with other solvents (petroleum spirit, acetone, and absolute alcohol), have been separated and isolated in a fairly pure state by the Tswett chromatographic method. They were identified as lycopene and β-carotene, which was confirmed by spectroscopic methods. S. G. S.

Determination of Butyric Acid in Wine and Vinegar. L. Klinc. (*Z. Unters. Lebensm.*, **1935, 69, 363–369.**)—A method previously described (*Biochem. Z.*, **1934, 273, 1**) has been adapted to the determination of small amounts of butyric acid in wine and vinegar. The method determines the total butyric acid (*i.e.* the normal and *iso*-acids), but normal butyric acid occurs in wine only in very small amounts. The special reagents required are: (1) 1·5 g. of ferric ammonium sulphate in 1 l. of 2 N sulphuric acid; (2) 3 per cent. hydrogen peroxide solution; (3) Scott Wilson's reagent (10 g. of mercuric cyanide and 180 g. of sodium hydroxide, each in 600 ml. of water, the solutions being mixed and cooled, and treated with a solution of 2·9 g. silver nitrate in 400 ml. of water. The solution is clear in about a day and is stable if kept in the dark). (4) Acetone stock solution:—0·5 ml. of acetone is diluted with water and distilled. In a portion of the distillate the acetone is determined iodimetrically and another portion, corresponding with 100 mg. of acetone, is diluted accurately to 1 l. with 0·25 N sulphuric acid. (5) Acetone comparison solution: prepared as required from the stock solution by ten-fold dilution. All reagents must be free from chloride. A blank determination is made by distilling a mixture of 3 ml. of the acid iron solution (1) and 5 ml. of the hydrogen peroxide solution (2) from the flask A (which is attached directly to the condenser, without the flask B), until only about 0·5 ml. of residue remains. Five ml. of Scott Wilson's reagent (3) are added to the distillate, and if a slight blue opalescence appears, allowance must be made for it subsequently by standardisation against solutions of butyric acid of known strength. Wines are usually free from chlorides; if these occur they must be removed in the usual manner by means of silver sulphate and subsequent distillation. Forty ml. of filtered wine are mixed with 10 ml. of 20 per cent. phosphoric acid and about 50 ml. of water in a 500-ml. Kjeldahl flask, and distilled down to a residue of 8 to 10 ml. The distillate is received in a vessel containing 2 ml. of N sodium carbonate solution (which is usually sufficient to keep the distillate alkaline to litmus), and is afterwards made up to 100 ml. and divided into 4 equal portions, each of which is evaporated to dryness on the water-bath. One of the residues is dissolved in 2 to 5 ml. of water, 3 ml. of the acid iron solution are added, and the mixture is rinsed into flask A with 5 ml. of hydrogen peroxide solution. The distillation is carried out as in the blank determination. If no butyric acid is present, the distillate remains clear. A grey turbidity may form with quantities exceeding 50 mg. of acetic acid, and a white turbidity or a white precipitate with propionic acid and butyric acid. To distinguish between these the distillate is redistilled, the receiver being washed into flask A with 5 ml. of hydrogen peroxide solution. Flask B contains a boiling 30 per cent. solution of sodium hydroxide. The acetaldehyde (due to propionic



acid) is destroyed in flask B, whilst acetone passes over into the receiver which, as before, contains 5 ml. of Scott Wilson's reagent. All the acetone is present in the first ml. of the distillate. With 0·008 to 0·4 mg. of butyric acid a blue opalescence is produced; with 0·05 to 0·5 mg. a bluish-white or white turbidity; and with greater amounts a white precipitate. The remaining three dry residues are used for the quantitative determination, which is carried out in the same way. The butyric acid is determined nephelometrically as follows:—To three test-tubes, each containing 5 ml. of Scott Wilson's reagent, are added, respectively, 0·25 ml., 0·5 ml., and 1·0 ml. of the acetone comparison solution. The acetone solution is added in such a manner as to form a layer above the heavier liquid, and the addition should be made when the actual distillation begins. When a definite ring has formed between the two layers the tubes are gently shaken, and, when distillation is complete, their contents are diluted to the same volume as the distillate and compared against a dark background. The acetone comparison solution contains 0·01 g. of acetone per ml., and 0·25 ml. corresponds with 0·01 mg. of butyric acid. If the qualitative examination gave a turbidity, a micro-iodimetric determination is carried out as follows: The oxidation and re-distillation are carried out as in the qualitative test, but the Scott Wilson reagent is replaced by alkaline iodine solution (2 ml. of 0·005 *N* iodine in potassium iodide solution and 5 ml. 2 *N*-sodium hydroxide solution). After the re-distillation the condenser is rinsed out, and the distillate is allowed to stand for a short time. With relatively large amounts of butyric acid the iodoform is visible as a turbidity. The liquid is transferred to a beaker, acidified with 7 ml. of 2 *N* sulphuric acid, and the uncombined iodine is titrated back with 0·005 *N* sodium thiosulphate solution, starch indicator being added near the end-point. The value obtained is deducted from a blank determination carried out by distilling the stated amounts of Scott Wilson reagent and hydrogen peroxide into the alkaline iodine solution (1 ml. of 0·005 *N* iodine multiplied by 0·27, the amount of butyric acid in mg.). Results are given for a number of wines of widely different origins, varying in alcohol-content from 9 to 11 per cent. by volume, and in volatile acid content from 0·6 to 0·8 g. per l. The amounts of butyric acid found varied from 10 to 20 mg. per l.

For the determination of butyric acid in vinegar, 10 ml. of the filtered sample, 30 ml. of water, and 10 ml. of 20 per cent. phosphoric acid are distilled into an amount of *N* sodium carbonate solution equivalent to the free acid in the vinegar. The condenser should dip into the carbonate solution and the distillation should be continued until a residue of about 5 ml. remains. The distillate is made faintly alkaline and diluted to 100 ml., and the procedure used for wines is followed. Examination of 17 samples of vinegar showed that wine vinegar contains over 50 mg. of butyric acid per l., which indicates that butyric acid is formed during acetous fermentation. If the butyric acid content falls below this value, adulteration may be suspected. Spirit vinegar may contain up to 30 mg. per l. and, when the vinegar is decomposed the butyric acid may rise to about 50 mg. per l. Wine vinegars, however, do not fall below 50 mg., and may reach 290 mg. per l. The butyric acid content is therefore of some value in the detection of the adulteration of wine vinegars.

A. O. J.

Extractives of Capsicum. H. Berry. (*Pharm. J.*, 1935, **135**, 12.)—Capsicum of the B.P. standard was extracted with ether in a Soxhlet extractor. The residue from the ethereal solution was fractionated into two parts (A and B) by treatment with alcohol (90 per cent.). The ether-exhausted marc was then percolated with alcohol. Evaporation of the percolate gave a red liquid, C. When the exhausted marc was treated with water and the percolate evaporated to dryness, another fraction, D, was obtained. Fraction A (7·8 per cent.) was very pungent and soluble in ether and alcohol; B (9·8 per cent.) was non-pungent and soluble in ether but insoluble in alcohol; C (7·3 per cent.) was non-pungent and insoluble in ether, but soluble in alcohol; D (7·5 per cent.) was non-pungent, insoluble in ether and alcohol, but soluble in water. Another portion of the same sample of capsicum was extracted with cold alcohol. On evaporating off the alcohol a dark red semi-solid residue (from which a dark red oil separated) was obtained. About 70 per cent. of this was soluble in ether, the remainder being a non-pungent resinous mass. When the alcohol-exhausted marc was extracted with ether an oil similar to B was obtained. Capsicum seeds gave a yellow non-pungent oil on extraction. The British Pharmaceutical Codex Pharmacy Sub-committee therefore recommended that the oleoresin of capsicum be prepared by percolation with ether, followed by treatment of the residue from the ethereal solution with alcohol (90 per cent.). This gives a product that is at least three times as strong as the oleoresin of the B.P.C. 1923, and is also soluble in ether, alcohol (90 per cent.), chloroform, benzene, petroleum spirit, fixed oils and turpentine. S. G. S.

The Red Pigment in the "Perfection" Pimento (*Capsicum Annuum*). W. L. Brown. (*J. Biol. Chem.*, 1935, **110**, 91–94.)—The red colouring matter of the "Perfection" pimento has been isolated by the method of Zechmeister and von Cholnoky (*Ann. Chem.*, 1931, **489**, 1), and found to be identical with capsanthin isolated from Hungarian paprika. S. G. S.

Colour Reaction of Chloral and its Application to the Identification of Syrup of Chloral. M. Pesez. (*J. Soc. Pharm. Chim.*, 1935, **127**, 68–69.)—Chloral may be identified by a reaction similar to that previously described for tartaric acid, which consists in the condensation, in concentrated sulphuric acid, of the products of decomposition of resorcinol and tartaric acid in the presence of nascent bromine. Two ml. of conc. sulphuric acid, 0·1 ml. of a resorcinol mixture (resorcinol, 2 parts; potassium bromide, 10; water 100 parts; and sulphuric acid 1 ml.), and 0·1 ml. of the chloral solution are warmed, when a yellow-pink colour develops, becoming violet at about 90° C. and blue at 100° C. If the chloral solution is sufficiently concentrated, there is formed a white precipitate of para-chloral which disappears at 10° C. The reaction is similar in all respects to that of tartaric acid, and may be applied to syrup of chloral by adding to 1 ml. of the syrup 5 ml. of water and 2 ml. of ether. After being shaken and left for a few seconds the ethereal layer is pipetted off into a test-tube, which is held in boiling water and shaken and warmed alternately until the ether has evaporated. The 2 ml. of sulphuric acid are then added, and the reaction proceeded with as before.

The characteristic blue colour appears after 2 to 3 minutes' heating. Under these conditions syrup of tartaric acid gives a negative result, owing to the insolubility of tartaric acid in ether. D. G. H.

Determination of Bismuth in Medicinal Substances. J. Gonzalez-Carrero. (*Bull. Biol. Pharm.*, 1935, 181–182.)—To the solution of the substance (about 20 ml. containing 5 to 20 mg. of bismuth), acidified with nitric acid or sulphuric and tartaric acids, are added a few glass beads; the liquid is given a rotatory motion, and 2 to 3 ml. of a freshly prepared saturated solution of potassium chromithiocyanate ($K_3Cr(SCN)_6$) are added to precipitate the bismuth. After 3 minutes, 5 to 6 drops of toluene are added; the mixture is well shaken and filtered. The precipitate is washed (presumably with water) and is dissolved, by heating, in 10 to 15 ml. of "hydrolysing reagent" (Rochelle salt, 150 g.; sodium hydroxide, 108 g.; potassium bromide, 25 g.; water to 1,250 ml.). The green solution obtained is acidified with 10 to 15 ml. of conc. hydrochloric acid, and a slight excess of 0·1 *N* potassium bromate is added; after 1 minute about 1 g. of potassium iodide is added, and the liberated iodine is titrated with standard thiosulphate solution; 1 mg. of bismuth = 0·58 ml. of 0·1 *N* potassium bromate solution. S. G. C.

Spectrographic Absorption of Ergometrine in Relation to the B.P. Colour Test. N. L. Allport and S. K. Crews. (*Pharm. J.*, 1935, 135, 8–9.)—Aqueous solutions of ergometrine exhibit a blue fluorescence in daylight, and in filtered ultra-violet light this is more brilliant than that given by ergotoxine. A fairly pure specimen of ergometrine, consisting of very pale cream crystals, had m.p. 164° C., an alkaloid percentage of 178 (calculated as ergotoxine and determined by the Maurice Smith colour-test), and an E value of 185 at 316 $m\mu$ in a 0·006 per cent. solution. All determinations made by the modified Maurice Smith test gave over 100 per cent. of alkaloid calculated as ergotoxine, indicating either a lower molecular weight for ergometrine or a greater proportion of the indole residue in the molecule. A parallelism exists between the magnitude of the extinction coefficient and the figure derived from the colour-test. With *p*-dimethylaminobenzaldehyde as a reagent the blue colour was given both by ergometrine and ergotoxine, and had a maximum absorption at 550 $m\mu$. Under the conditions of the B.P. colour-test both ergotoxine ethane sulphonate and ergometrine gave identical colours, with a maximum absorption at 580 $m\mu$. S. G. S.

Distinction between Chloroform and Carbon Tetrachloride. N. Schoorl. (*Pharm. Weekblad*, 1935, 72, 751.)—Quinine sulphate may be used in place of papaverine hydrochloride in the test described by Rozeboom (ANALYST, 1935, 560), but it is preferable to apply the two following reactions, which are positive for chloroform and for carbon tetrachloride, respectively:—(1) Chloroform reduces boiling Fehling's solution, carbon tetrachloride does not. (2) One drop (not more) of the sample is heated in a test-tube which is loosely closed with a cork. The vapour of carbon tetrachloride (not that of chloroform) is oxidised to carbonyl chloride and chlorine, and the latter may be identified by means of the starch and potassium iodide reaction in the solution obtained by shaking the cooled residue with 1 ml. of water. J. G.

Volumetric Determination of Sodium Glycerophosphate. S. Babitsch. (*Z. anal. Chem.*, 1935, **101**, 398–401.)—Sodium glycerophosphate (0·1 to 0·2 g.) is dissolved in water (20 to 25 ml.). The solution is treated with 5 to 10 ml. of 0·5 *N* lead nitrate solution, and boiled for 5 to 10 minutes. After cooling, the volume is adjusted to 50 ml., and the liquid is well stirred. The excess of lead is determined in 25 ml. of filtrate. This may be done by addition of 5 drops of phenolphthalein indicator, boiling, and titration with 0·1 *N* sodium carbonate solution to a decided pink tinge. The solution is again heated to boiling, and, if the colour disappears, a little more soda solution is required. One ml. of 0·1 *N* lead solution is equivalent to 0·013508 g. of $C_3H_5(OH)_2.PO_2(ONa)_2.3H_2O$, or 0·010808 g. of the anhydrous salt. The result is not affected by sodium cacodylate. Calcium glycerophosphate is not quantitatively decomposed under the above conditions. W. R. S.

Biochemical

Reactions of Dyes with Cell Substances. (I) Staining of Isolated Nuclear Substances. E. G. Kelley and E. G. Miller. (*J. Biol. Chem.*, 1935, **110**, 113–117, 119–140.)—(I) Starting from beef thymus, β-nucleohistone, α-nucleoprotein, nucleic acid, histone, and metaprotein were prepared. These were attached to a microscope slide by dropping a fine suspension on to a slide previously smeared with Mayer's albumin solution, and drying at 50° C. After 2 hours the smears were washed in running water or buffer solution for 2 hours, then immersed in the dye solution for 5 minutes, and again rinsed in water or the buffer. Fixations and stainings were made at the same *p*H, the *p*H values used being 2, 6, 8·5, and 10. The stained smears were examined immediately after staining, and again after mounting in balsam. Parallel stains were also made on paraffin-imbedded sections of thymus tissue. The stains used were thionine, light green S.F., haematoxylin (with and without a mordant), and Feulgen stain (with and without hydrolysis). Each of these was also treated with phosphotungstic acid, mercuric chloride, formaldehyde, and 95 per cent. alcohol as fixatives. A table is given showing the results obtained. With unmordanted haematoxylin the colours obtained were dependent upon the *p*H values.

(II) Differential Staining of Nucleoprotein and Mucin by Thionine and Similar Dyes. The dyes examined, which on dilution showed a shift of maximum light absorption toward the longer wave-lengths, gave a colour difference between nucleoproteins and mucin parallel to that obtained by the usual thionine or toluidine technique of histological examination. The colour of the stained mucin corresponds with that of the dye in concentrated aqueous solution, and the colour of the nucleoprotein with that of the dye in dilute solution. Change of *p*H does not affect this reaction. It is suggested that the phenomenon at work here is the same as that involved in the dilution-shift of absorption maxima. S. G. S.

Determination of very small Proportions of Ethyl Bromide in Biological Media. F. L. Hahn. (*Compt. rend.*, 1935, **201**, 296–298.)—Ethyl bromide held by animal tissue may be totally expelled in a current of air and steam, and, if the gases are then passed through a red-hot quartz tube, the ethyl bromide is entirely decomposed, and the bromine may be condensed as hydrobromic acid. A slight excess of sodium hydroxide is added, followed by dilute acetic acid (with methyl red as indicator) to neutralise the solution, and the bromine is then determined by the introduction of chloramine and fluorescein, resulting in the formation of eosin, the colour of which is compared with those of prepared standards, which may conveniently represent 0, 2, 5, 10 γ etc. of bromine. About 14 ml. of distillate may be obtained in 30 minutes, and this will contain approximately the whole of the bromine. The experimental error is not more than 5 per cent. D. G. H.

Liberation of Methyl Sulphide by Seaweed. P. Haas. (*Biochem. J.*, 1935, **29**, 1297–1299.)—The seaweeds *Polysiphonia fastigiata* and *P. nigrescens* were found to evolve a penetrating, sickly odour on drying. This has been identified as methyl sulphide which is given off by the plant. The bromine derivative of this substance, originally prepared by Cahours in 1875 (*Compt. rend.*, **60**, 650), has again been prepared from the methyl sulphide obtained from these algae, and its m.p., which is recorded for the first time, is 93—94° C. S. G. S.

Determination of Iodine in Biological Material. V. Trevorrow and G. J. Fashena. (*J. Biol. Chem.*, 1935, **110**, 29–38.)—For the determination of the iodine-content of blood, 15 ml. of oxalated blood are treated with 15 ml. of water, 30 g. of solid potassium dichromate and about 10 mg. of cerous sulphate, and 80 to 100 ml. of chromic and sulphuric acid mixture (3 g. potassium dichromate in 5 ml. of water dissolved in 95 ml. of concentrated sulphuric acid) are added slowly, the flask being cooled in water and the contents mixed by gentle rotation. After the reaction has subsided, the flask is heated over a free flame, until digestion is complete and foaming has ceased, and is then cooled. A few pieces of broken, unglazed earthenware and 25 ml. of water are added, and the mixture is boiled vigorously until the volume is equal to that left after digestion. During this boiling the escaping vapour has the odour of acetic acid. If this odour persists after boiling, the process must be repeated until the odour of acetic acid is no longer detected. The mixture is now cooled to 50—55° C., and 4 ml. of phosphorous acid are added (an A.R. grade is melted, a minimum amount of water is added to prevent solidification, and the mixture is steam-distilled, the volume being kept constant, until free from chloride). The sides of the flask are washed down with a minimum amount of water, and the solution is steam-distilled in a special all-glass apparatus into a receiver containing 10 ml. of a 0·1 per cent. solution of potassium carbonate, a pressure of about 65 cm. of mercury being used. After 40 ml. have been condensed (25 to 30 minutes) the fluid in the receiver is transferred to a 125-ml. Pyrex Erlenmeyer flask, 3 drops of a 10 per cent. solution of sodium sulphite and 2 drops of a 0·01 per cent. solution of methyl orange are added, and the mixture is made just acid by the careful addition of 3 per cent. sulphuric acid, boiled for one minute, and cooled. If, as is usually the case, the solution has become alkaline, more acid is added and the solution again boiled. Bromine vapour is now added to the acid solution and should produce an immediate decolorisation of the methyl orange. The solution is concentrated to 2 ml. by boiling and cooled, 2 drops of starch solution and a few crystals of potassium iodide are added, and the liquid is titrated with 0·001 *N* sodium thiosulphate solution, using a micro-burette. For substances other than blood, the amounts of potassium dichromate and sulphuric acid must be varied. About 10 g. of dichromate and 30 ml. of chromic-sulphuric acid are required per g. of dried protein; 20 g. of dichromate and 40 ml. of the acid mixture for each g. of pure butter fat; and 7 g. of dichromate and 25 ml. of acid for each g. of carbohydrate. S. G. S.

Chemistry of the White Rots of Wood. The Effect on Wood Substance of *Ustulina vulgaris* Tu. W. G. Campbell and J. Wiertelak. (*Biochem. J.*, 1935, **29**, 1318–1321.)—When *Ustulina vulgaris* Tu. lives as a parasite on lime wood (*Tilia vulgaris*, Hayne) it produces a decomposition of the white-rot type, although the chief source of its nourishment is the carbohydrate portion of the cell wall. Lignin is also decomposed, but not to the same extent as the Cross and Bevan cellulose. The saprophytic action of this fungus on beech wood is of the same order as its parasitic action, but is much slower. The mechanical properties of lime wood are affected to a considerable extent by the fungal action. S. G. S.

Ascorbic Acid (Vitamin *C*) Oxidase. H. Tauber, I. S. Kleiner and D. Miskind. (*J. Biol. Chem.*, 1935, **110**, 211–217.)—An enzyme which has been isolated from the pericarp of the Hubbard squash (*Cucurbita maxima*) differs from that found in cabbage leaves by Szent-Györgyi (*Science*, 1930, **72**, 125; *J. Biol. Chem.*, 1931, **90**, 385). The new enzyme oxidises 100 per cent. of the substrate (synthetic and natural *l*-ascorbic acid) rapidly, and its kinetics are those of a single enzyme. It appears to be specific for ascorbic acid, as it does not affect phenols, glutathione, cysteine or adrenalin. This oxidase is inactivated by trypsin, which indicates that it is either a protein or has protein as an indispensable constituent. The rôle of the enzyme in the physiology of the plant is obscure, but there is practically no ascorbic acid (reduced or oxidised) present in the fruit. It is possible that it plays a part in the early processes of ripening, or that it is stored in the fruit for use by the leaves. S. G. S.

Sensitive Spot Reaction for Ascorbic Acid (Vitamin *C*). H. Tauber. (*Mikrochem.*, 1935, **17**, 111–112.)—This reaction depends on reduction of potassium ferricyanide by an acid solution of ascorbic acid and conversion of the resulting ferrocyanide into Prussian blue. The reagents required are: (1) 8 per cent. acetic acid solution; (2) 1 g. of anhydrous ferric sulphate dissolved by boiling with 80 ml. of water and 18 ml. of 85 per cent. phosphoric acid, and 1 per cent. potassium permanganate solution then added dropwise to give a faint pink colour; after being boiled for a few minutes, the liquid is filtered, cooled, and diluted to 100 ml.; (3) 0·4 per cent. potassium ferricyanide solution. A mixture of 1, 2, and 3 in equal volumes should give no blue colour.

A few grams of the vegetable or animal tissue to be tested are macerated with 2 to 3 times the quantity of hot solution (1) in a test-tube by means of a sharp-edged glass rod, a drop of the extract being placed on a double filter-paper. The drop on the lower paper is then treated with a drop of (3) and a drop of (2). With more than 0·005 mg. of ascorbic acid in 0·05 ml., a blue colour shows immediately, whilst if 0·003 mg. is present, the colour appears within 30 seconds. Ascorbic acid is almost always present in tissues in the reduced form, but any oxidised form may be reduced by means of hydrogen sulphide, excess of which is then expelled by a current of nitrogen. Uric acid does not disturb this reaction, and sugar solutions interefere only if they have been previously boiled with alkali. Large amounts of cysteine, glutathione, or pyrogallol, but not the quantities normally present in tissues, affect the reaction. In important cases, biological confirmation is necessary. T. H. P.

Bacteriological

Intense Development of the "Tourne" Bacterium in a Highly Alcoholic Medium. L. B. D'Estivaux. (*Ann. Falsif.*, 1935, **28**, 288–290.)—A port wine, containing 16·8 per cent. of alcohol and having a marked acid taste, was found to contain 1·86 g. of volatile acid per l. The wine contained a few atrophied yeast cells and a large number of long, filamentous, gram-positive bacteria, which multiplied rapidly in yeast water-sucrose. A year later (in 1934) the same organism was found in wines of 15 per cent. alcoholic strength and, during the hot season, in liqueur wines with 18 per cent. of alcohol. The wines developed increasing turbidity, which settled after some months, the deposit being virtually a pure culture of the filamentous bacteria; the volatile acidity was increased from 0·27 to 0·66. In the wine the bacteria formed curved, intertwined growths. When plated out on gelatin medium, they formed short rods which, when grown in yeast water containing 3 per cent. of sucrose, gave highly motile, L-shaped doublets. In yeast water containing 17 per cent. of alcohol growth was slow and gave at first the same L-forms. Later, however, butyric acid suddenly developed, with evolution of gas, and the organisms again assumed a long, filamentous form, less curved than in the wine-deposits. Unlike nearly all bacteria which bring about "tourne" in wines, the present organism gave no mannitol under any conditions. T. H. P.

Agricultural

Use of *Aspergillus niger* in Testing Potash Availability [in Fertilisers]. L. D. Haigh. (*J.A.O.A.C.*, 1935, **18**, 293–297.)—The Niklas method of testing the availability of the potash of soils as a plant food is virtually a citric acid extraction of the potash, the amount extracted being gauged by the subsequent growth of *Aspergillus niger*. Adaptation of this method to the testing of the availability of potash in fertiliser mixtures necessitates some modification, since, if growth of the mould is to be the index of availability, extraction by acid should be avoided. In the author's tests, therefore, citric acid was omitted from the nutrient solution, which was sterilised before addition of the *Aspergillus* spores. The weights of mycelium obtained from the nutrient solutions containing various proportions of water-insoluble fertiliser residues were compared with those obtained from the same nutrient solutions containing water-soluble potash (as K_2SO_4) in various amounts. Control experiments were made with nutrient solutions containing no potash.

A mixed fertiliser containing a certain amount of an 18 per cent. superphosphate, together with water-soluble potassium salts, was found to contain 0·31 per cent. of water-insoluble K_2O, whereas the water-insoluble K_2O supplied by the superphosphate was only 0·24 per cent. This disparity is regarded as due to adsorption of water-soluble K_2O, which would thus appear as water-insoluble. In the mould-growth experiments, the greatest growth was produced by the more readily available water-soluble potash and the least by the water-insoluble potash of the extracted superphosphate residue. The potash in the water-insoluble residue of the mixed fertiliser gave an intermediate result, probably because the adsorbed potash of this residue was more readily available than the potash in the superphosphate residue.

A disturbing factor in this use of *Aspergillus* is the development of acidity in the nutrient solutions as growth of the mould proceeds. The acid thus formed tends to dissolve more potash, which the mould absorbs readily, the stimulated growth resulting in further development of acidity, and so on. Further work is necessary to devise means of controlling the acidity, but the results recorded indicate that, in a modified form, the method may be useful in distinguishing between insoluble forms of potash of different degrees of availability. T. H. P.

Determination of Iodine in Soils. G. S. Fraps, J. F. Fudge and E. C. Carlyle. (*J.A.O.A.C.*, 1935, **18**, 314–315.)—The fusion method of determining iodine in soils (*cf.* von Fellenberg, *Biochem. Z.*, 1924, **152**, 116; McHargue, *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 214) consists briefly of the following steps: fusion of the soil with potassium hydroxide; treatment of the melt with water, acidification with hydrochloric acid, rendering slightly alkaline, filtration and evaporation; separation of the potassium chloride with alcohol, evaporation of the alcoholic extract, dissolution of the residue, treatment of the solution with acid and sodium nitrite to liberate the iodine, extraction of the iodine with carbon disulphide, and colorimetric comparison with a standard solution. The method is not found to give concordant results, but these are obtainable when various suggested modifications in procedure are introduced. Further examination of the method is, however, considered necessary. T. H. P.

Organic

Organic Matter in Sea-water. L. Espil. (*Bull. Soc. Chim.*, 1935, **2**, 1007–1012.)—Sea-water at various places near the coast has been found to contain an appreciable content of organic matter. The amount appeared to vary with the time of year, as much as 200 mg. per l. of organically combined carbon having been found during the autumn months, compared with 1 mg. per l. for water from the open sea. For the determination of the carbon, the water was evaporated to dryness; the residue was treated with sufficient hydrochloric acid to decompose carbonates and bicarbonates, and dried at 80 to 100° C. A current of carbon-dioxide free air was then passed through the mass, the temperature of which was gradually raised to 160 to 200° C. The issuing gas was passed through baryta solution to absorb the carbon dioxide given off in the oxidation of the organic matter; the barium carbonate was subsequently filtered off, and the carbon dioxide was determined by titration with acid. Attempts were made to isolate the organic matter from sea-water by extraction with solvents, *e.g.*, trichloroethylene. Whilst the amount of material obtained was insufficient for satisfactory identification, it appeared to consist of at least two substances, which in ultra-violet light gave, respectively, a yellowish-green and orange-red fluorescence. It was considered that the presence of the organic matter was of significance in connection with the life of marine fauna. S. G. C.

Determination of Small Amounts of Methyl Alcohol in Presence of Ethyl Alcohol and its Homologues in Large Quantities. M. Flanzy. (*Ann. Falsif.*, 1935, **28**, 260–277.)—The method described comprises the following operations: (1) Conversion of the primary alcohols into the corresponding iodides by treatment with hydriodic acid; (2) fractional entrainment of the alkyl iodides in a current of carbon dioxide; (3) regeneration of the alcohols by treatment of the aqueous solutions of the iodides with silver acetate, the silver iodide formed being weighed; (4) oxidation of the alcohols by means of cold potassium dichromate and sulphuric acid, the amount of oxygen consumed being determined. The exact conditions to be adhered to in each step of the process and the methods of calculation employed are described in detail. The method is long, and does not lend itself to adequate description in an abstract. The results obtained by its application to a number of wines and spirits are given. T. H. P.

Fatty Acids of Japan Wax. M. Tsujimoto. (*J. Chem. Soc. Japan*, 1935, **10**, 212–219.)—The examination of the component fatty acids of unbleached Japan wax (fruit coat fat from the berries of "Hazé" *Rhus succedanea*) and containing no kernel oil shows the approximate composition to be palmitic acid 77, stearic and arachidic 5, oleic 12, linolic less than 1, and dibasic acids 6 per cent. Hexadecenoic and linolenic acids are probably absent. The fat from which the acids were prepared was a brownish-yellow solid, of m.pt. 53—53·5° C. sp. gr. 99/4°, 0·8608, saponification value, 208·1; iodine value, 13·4; Reichert-Meissl value 0·30; acid value, 15·9; and unsaponifiable matter, 0·77 per cent. The fatty acids formed a brownish-yellow crystalline mass having m.p. 63° C.; iodine value, 12·7; neutralisation value, 215·3 and containing 6·3 per cent. dibasic acids. The acids were crystallised from acetone, and the liquid acids were separated from the final filtrate by the lead salt and ether method. The methyl esters of the mixed fatty acids were distilled in batches and the fractions obtained redistilled and examined for their component fatty acids. From an examination of the free fatty acids it is concluded that their components are nearly the same as those of the mixed acids of the wax, but a larger proportion of oleic acid is present. It is noted that, although myristic acid could not be detected in Japan wax, it occurs abundantly in the wax of "Tsutaurishi" *Rhus toxicodendron*, var. *vulgaris*. D. G. H.

Shark-liver Oils. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 272–273B.)—The present paper is additional to others on shark-liver oils, and supplies supplementary information concerning 8 shark oils. Of these, "Aizamé" is probably intermediate between *Centrophorus acus* Garman and *Centrophorus atromarginatus* Garman, but the species could not be identified.

	Liver oil from	Sp. gr. at 15°/4° C.	n_D^{20}	Acid value	Saponification value	Iodine value (Wijs)	Unsaponifiable matter Per Cent.	Crude squalene* Per Cent.	$SbCl_3$ test
(1)	Aizamé, No. 1	0·8643	1·4924	0·18	22·5	329·6	89·20	84·8	Light blue
(2)	,, No. 2	0·8680	1·4909	0·17	32·4	314·5	83·50	77·8	,, ,,
(3)	,, No. 3	0·8692	1·4900	0·17	37·2	307·3	81·19	75·9	,, ,,
(4)	Zaraka (Momijizamé)	0·8820	1·4842	0·17	80·8	235·8	55·87	50·8	,, ,,
(5)	Togaritsunozamé (adult)	0·9124	1·4780	0·75	174·8	154·4	5·34	Absent	Blue
(6)	,, (young)	0·9219	1·4778	0·53	178·3	151·8	2·71	,,	Light blue
(7)	Cat-shark (Male)	0·9221	1·4760	0·70	183·4	135·5	2·35		Pale blue
(8)	,, (Female)	0·9254	1·4780	0·24	179·2	149·9	3·88		
(9)	Gaikotsuzamé	0·9213	1·4762	1·07	179·8	140·6	1·91		
									Light blue
(11)	Porbeagle	0·9289	1·4824	1·34	181·5	187·2	2·51		
(12)	Hammerheaded shark	0·9304	1·4855	1·24	174·4	202·0	3·98	,,	Deep blue

* It contained a small proportion of pristane, and probably also of other hydrocarbons.

Arizamé and zaraka liver oils gave copious white precipitates in the antimony trichloride test, probably due to unsaturated terpene hydrocarbons. D. G. H.

Whale-shark Liver Oil. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1935, 38, 271–272B.)—The whale-shark (*Rhidonon typicus* Smith) was 5·8 m. long and the liver, from a specimen which had probably died from starvation, weighed 68 kg. and was of a greyish-white colour and not oily in appearance. From 10 kg. of liver, 5·49 kg. of a pale brownish-orange, soft oil were obtained, which became clear above 40° C., and gave a faint bluish-violet colour in the antimony trichloride test. It had the following characteristics: Sp.gr. at 40/4° C., 0·8977; saponification value, 182·5; iodine value (Wijs), 108·6; Reichert–Meissl value, 0·11; acid value, 25·0; unsaponifiable matter, 5·04 per cent. The fatty acids had m.p., 41–42° C.; iodine value, 116·7; and neutralisation value, 201·4; and yielded 27·8 per cent. of ether-insoluble bromides containing 70·23 per cent. of bromine. By the lead salt and ether method 40·9 per cent. of white crystalline solid acids were obtained, having m.p. 51–52° C.; iodine value, 18·0, and neutralisation value, 213, and 59·1 per cent. of orange-yellow liquid acids of n_D^{20}, 1·4710; iodine value, 177·6; and neutralisation value, 191·4. The lithium salt and acetone method gave 19·5 per cent. of highly unsaturated acids of n_D^{20}, 1·4880; iodine value, 330·5; and neutralisation value, 167·0. The fatty acids are regarded as consisting mostly of C_{10}—C_{22} acids, with C_{16} and C_{18} acids predominating, and the C_{20} and C_{22} acids are probably highly unsaturated. Palmitic acid is the main component of the solid acids. The unsaponifiable matter was a hard crystalline orange-yellow solid, with iodine value 89·9. It gave a deep blue colour with antimony trichloride, and its main constituent was 43·8 per cent. of cholesterol, but selachyl alcohol was identified, and batyl alcohol was probably present. D. G. H.

Determination of Citronellal in Java Citronella Oil. P. A. Rowaan and D. R. Koolhaas. (*Chem. Weekblad*, 1935, 32, 405–406.)—A known weight (*x* g.) of the sample (approx. 2 g.) is weighed with an accuracy of 1 mg. into a 150-ml. flask, and 10 ml. of 95 per cent. alcohol and 20 drops of a 0·1 per cent.

solution of bromphenol blue in alcohol are added. The mixture is neutralised with 0·1 *N* potassium hydroxide solution, 20 ml. of a 0·5 *N* solution of potassium hydroxide in alcohol being then added, followed immediately by 20 ml. of a 5 per cent. solution of hydroxylamine hydrochloride in alcohol, which are added from a measuring cylinder. The mixture is shaken well and allowed to stand at room temperature for 1 hour (in Europe) or 15 minutes (in the Tropics), and is then back-titrated with a 0·5 *N* solution of hydrochloric acid in alcohol to a green-yellow colour. If the strength of the acid is nN, and the back-titration, after making allowance for any blank, is a ml., then the percentage of citronellal is $15{\cdot}4\, na/x$. This procedure is preferred to existing methods (*cf.* Rowaan, *id.*, 1932, **29**, 603; and Zimmermann, *Perf. and Ess. Oil Record*, 1932, **23**, 128), and it is claimed that it is simpler to operate than that adopted by the S.P.A. Standing Committee on Uniformity of Analytical Methods (ANALYST, 1932, **57**, 773), and that the indicator gives a sharper end-point (*cf.* Schultes, *Z. angew. Chem.*, 1934, **47**, 258). J. G.

Determination of *o*-Phenylphenol. W. O. Emery and H. C. Fuller. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 248.)—The method depends on the precipitation of an insoluble red compound when *o*-phenylphenol reacts with iodine. To the slightly alkaline aqueous solution of *o*-phenylphenol (about 200 mg. in 200 ml. of water) are added 2 g. of sodium carbonate and 0·2 g. of sodium bicarbonate (to convert any sodium hydroxide into carbonate). The solution is warmed, and 0·2 *N* iodine solution is added in 10-ml. portions from time to time until, after being heated for 15 to 20 minutes on a steam-bath, the mixture shows a permanent yellow colour indicating an excess of iodine. Sufficient sulphur dioxide is added just to discharge the yellow colour; the precipitate is allowed to settle, filtered off on a Gooch crucible, washed with hot water, dried at 100° C., and weighed. One mol. of *o*-phenylphenol yields one mol. of iodine compound $C_{12}H_7IO$. *o*-Cresol may be determined in a similar manner, the product having the composition C_7H_5IO. S. G. C.

Determination of Naphthalene by Means of Picric Acid. A. P. W. Münch and R. T. Heukers. (*Chem. Weekblad*, 1935, **32**, 411–414.)—The reaction between naphthalene and picric acid may occur in two distinct ways (after the principles of van't Hoff and Le Chatelier, and of Henry, respectively): *viz.* (1) in the vapour state, the resulting vapour of naphthalene picrate dissolving and eventually forming solid naphthalene picrate, which attains an equilibrium with its own vapour phase; (2) the naphthalene vapour may dissolve and react with picric acid in solution to form solid naphthalene picrate, which eventually attains an equilibrium with its vapour as in (1). These alternatives are made the basis of a theoretical deduction of the optimum conditions for this determination, and it is demonstrated that it is not possible by means of picric acid to reduce the vapour-pressure of naphthalene to a value below that of the equivalent of solid naphthalene picrate. A 100 per cent. yield of naphthalene picrate is possible only at temperatures at which the vapour-pressure of this substance in the solid state is zero; this vapour-pressure is appreciable, however, even at 12° C. (*cf.*

Seebaum and Oppelt, *Gas Wasserfach*, 1934, 77, 280; van Dijk. *Chem. Weekblad*, 1935, 32, 111). The yield is considerably greater at 2° C. than at 12° C., but as benzene also forms a solid compound with picric acid at this temperature, it is considered that for work in connection with the gas-works products it is more desirable to work at 12° C. and to allow for the lower yield (90 to 95 per cent.); moreover, at this temperature the influence of the presence of any solid picric acid is less. The vapour-pressure of benzene picrate at 12° C. is greater than that corresponding with the partial pressure of benzene in a normal illuminating-gas. The naphthalene picrate may be determined by titration of the picric acid in solution with sodium thiosulphate before and after removal of the precipitate by filtration. Alternatively, the precipitate may be removed by filtration, washed and dissolved in hot water, and the picric acid produced by decomposition in this way is then titrated. The respective drawbacks are the difficulty of obtaining duplicate titrations which are exactly concordant, and of washing out the last traces of picric acid without dissolving the precipitate. The latter difficulty may be overcome by washing until the yellow colour is no longer pronounced in the filtrate, and under such conditions the second method is preferred; the results are low, but they are consistently low and can be allowed for. An apparatus is described for the determination of the m.p. (116° C.) of benzene picrate, in which the sample is placed in the bottom of a narrow glass tube which is immersed in a bath of paraffin wax. The other end, which is also closed and contains pure benzene, is immersed in a second wax-bath having a slightly lower temperature; the solid and liquid are separated by a plug of cotton-wool in the bend of the tube, and a thermometer is placed close to the cotton-wool plug. J. G.

Structures of some Sandalwoods and their Substitutes, and other little-known Scented Woods. C. R. Metcalfe. (*Bull. Miscel. Information, Kew, No.* 4, 1935; *Perf. and Ess. Oil Record*, 1935, 26, 244–247.)—No reliable macroscopical differences exist, but it is comparatively easy to distinguish *S. album* (E. India) from *Eucarya spicata* (Australia) microscopically by means of the taller rays of the former; these two species yield most of the sandalwood of commerce. The number of vessels and rays in a unit area, and the dimensions of the radial and tangential vessels, and of the metatracheal parenchyma cells and the rays and ray cells are tabulated for *S. album, freycinetianum* Gaud. (Hawaii), *austrocaledonium* Vieill. (New Caledonia), and *Yasi* Seem. (Fiji), and for *Eucarya spicata, acuminata* Sprague et Summerhayes, and *Exocarpus latifolius* R. Br. (Australia). The most useful distinguishing feature is the height of the rays cells, and these usually fall within the ranges 160 to 360, 100 to 250, 100 to 200, 80 to 180, 100 to 230, 100 to 200, and 80 to 180μ, respectively. A unique characteristic of *S. freycinetianum* is the narrow and almost continuous concentric zones of (terminal) parenchyma. The vessels occur in groups more frequently in *Eucarya spicata* than in any other of the *Santalaceae* examined. Extracts of these woods in water or alcohol are colourless or pale yellow, but addition of ammonia produces a pale red-brown colour, and sometimes a fluorescence, with *S. album*; a more intense colour and a fluorescence with *S. freycinetianum*; and a pale lemon colour, sometimes with a faint green tinge, with the others, this tinge being always most intense in the case of the *Eucarya* and *Exocarpus* woods. The substitutes for sandalwood which are also discussed are *Eremophila Mitchelli* Benth. (budda or bastard Australian sandalwood), *Ximenia Americana* Willd., *Erythroxylum monogynum* Roxb., *Pterocarpus santalinus* Linn. f. (red sanders wood), *Adenanthera pavonina* L., and *Amyris balsamifera* L. (W. Indian sandalwood); it is considered that the last-named belongs to the *Rutaceae* rather than, as previously thought, to the *Burseraceae*. It is also considered that the sandalwood oils of E. African origin are mostly derived from members of the *Canellaceae* and from the genus *Brachylaena* (*Compositae*), but the exact botanical source is still uncertain. It was previously believed that certain scented woods from E. Africa and Madagascar were *Cinnamosma fragrans* (cf. *Perf. and Ess. Oil Record*, 1933, **24**, 75), but it is now shown that they belong to the closely-related genus *Warburgia*, which has very similar microscopical characteristics. Descriptions of *Convolvulus scoparius* L. (Canary rosewood), *C. floridus* L., and *Urandra.* sp. (daru-daru) are given, and photomicrographs are also included (*cf.* ANALYST, 1932, **57**, 124, 515).

J. G.

Inorganic

Detection of Cadmium as Selenide. P. Krumholz and O. Kruh. (*Mikrochem.*, 1935, **17**, 210–214.)—The precipitation of cadmium sulphide from an ammoniacal solution containing also a cyanide is not a very sensitive reaction, and is disturbed by the presence of either copper salts or oxidising agents. Precipitation of cadmium selenide (also in presence of ammonia and a cyanide), which has a deep reddish-brown colour, forms a more delicate means of detecting cadmium. The reagent is prepared by dissolving 1 g. of sodium selenide in a little hot water, diluting to 100 ml., and adding a concentrated solution of 0·5 g. of potassium cyanide. The filtered liquid is stable for a few days if stored in well-stoppered bottles in the dark. The procedure under various conditions is as follows.

(1) Two ml. of the solution to be tested, containing ammonia and ammonium salts, are heated to boiling-point in a 10-ml. test-tube with a drop of 25 per cent. potassium cyanide solution, and 5 drops of the reagent are added. The tube is cooled in water and its contents are well shaken with 1 ml. of ether. After separation of the layers, a reddish-brown film appears at the boundary if cadmium is present. Limiting sensitivity, 2·5γ; limiting concentration, 1 in 800,000. (2) In presence of copper, 2 ml. of the solution containing ammonia and ammonium salts are heated to boiling, and 25 per cent. potassium cyanide solution is added dropwise until the blue colour of the copper-ammine salt has completely disappeared. One or two drops more of the cyanide solution are added, and the liquid is boiled, treated with 5 drops of the reagent, cooled, and shaken with ether as before. Limit of sensitivity, 4γ of cadmium in presence of 12 times as much copper; limiting concentration, 1 in 500,000. (3) When nickel or cobalt is present, addition of potassium cyanide [as under (2)] is continued until a clear yellow solution of the complex cyanides results. As the complex nickel or cobalt cyanide disturbs the detection of cadmium, even after shaking with ether, water is introduced below the ethereal layer by means of a capillary pipette. The ethereal layer

is thus forced up and the reddish-brown precipitate becomes apparent at the ether-water boundary. Limit of sensitivity, 4γ of cadmium in presence of 5000 (2500) times this amount of nickel (cobalt); limiting concentration, 1 in 500,000. (4) In presence of zinc, the procedure is as under (1), the potassium cyanide being added until the grey zinc selenide is dissolved, the liquid being then cooled and shaken with ether. Limiting sensitivity, 5γ of cadmium in presence of 5000 times as much zinc; limiting concentration, 1 in 400,000. (5) In presence of copper, nickel, cobalt and zinc, 2 ml. of the solution, containing ammonia and ammonium salts, are treated dropwise at the boiling point with 25 per cent. potassium cyanide solution until a clear yellow liquid results. After further addition of 1 or 2 drops of the cyanide, the liquid is boiled and then treated with 5 drops of the reagent. If zinc is present in very large amount, it is precipitated (to gether with the cadmium) as selenide, but may be redissolved by adding more potassium cyanide solution, drop by drop. The liquid is afterwards cooled and shaken with ether. Limit of concentration, 1 in 400,000, and of sensitiveness 5γ of cadmium in presence of 2500 times this quantity of copper, 2000 of zinc, and 1000 each of cobalt and nickel. The test is less sensitive if carried out as a drop reaction on filter-paper, but it may be applied as a drop test if a test-tube of 1 ml. capacity is used.

T. H. P.

Determination of Lead in Glass. P. Drawe. (*Chem.-Ztg.*, 1935, 59, 488.)—One to 2 g. of the powdered glass is fused in a silver crucible with 5 g. of sodium hydroxide, the melt being stirred with a stainless-steel stirring rod. After cooling, the mass is dissolved in water, and the lead is precipitated with ammonium sulphide. The lead sulphide is filtered off, washed with hot water, and dissolved in *aqua regia*; any insoluble residue is removed by filtration and washed with slightly ammoniacal ammonium acetate solution to recover any lead sulphate present. The ammoniacal lead solution is boiled, and any further precipitate is filtered off.* The solution is acidified with acetic acid, and the lead is precipitated as chromate in the usual way and determined gravimetrically. The sodium hydroxide fusion process is stated to be preferable to attack with hydrofluoric acid, which introduces difficulty owing to insoluble fluorides being formed from calcium, etc., in the glass.

S. G. C.

[**Abstractor's Note.*—Any hydroxides of iron, aluminium, etc., precipitated at this stage would entrain lead, rendering further separation necessary.]

Iodine Method for the Determination of Oxides in Steel. T. E. Rooney and A. G. Stapleton. (*J. Iron and Steel Inst.*, May, 1935, Preprint No. 7.)—The method is a "residue method," and involves dissolving the steel in iodine in anhydrous methyl alcoholic solution, filtering off, igniting and weighing the insoluble residue, which is then examined for silica, oxides of iron, manganese and aluminium by recognised methods. The solution process and the various operations previous to the ignition require to be done in an atmosphere of pure nitrogen in the complete absence of moisture. This necessitates a special technique and apparatus, for the details of which reference should be made to the original paper. Residues of the order of 0·1 per cent. were obtained from carbonyl iron and a range of plain steels containing 0·1 to 0·6 per cent. of carbon. A typical residue weighed 0·0076 g. (isolated from 8·27 g. of steel) and contained the following: SiO_2, 0·0008 g.; Fe_2O_3, 0·0040 g.; Al_2O_3, 0·0015 g.; Mn_3O_4, 0·0010 g. S. G. C.

Determination of Cobalt as Hexamminecobaltous Iodomercurate. A. Taurins. (*Z. anal. Chem.*, 1935, **101**, 357–359.)—The method used by the author for the determination of copper, cadmium, and nickel (ANALYST, 1934, **59**, 434) can be applied to cobalt if the operation is carried out in an atmosphere of carbon dioxide to prevent oxidation of the cobalt in the ammoniacal liquor. The crystalline flesh-coloured precipitate is $[Co(NH_3)_6][HgI_3]_2$, and contains 4·45 per cent. of cobalt. The original paper should be consulted for working details. W. R. S.

Volumetric Determination of Beryllium and Silicon in complex Fluoride Solution. J. A. Tschernichow and E. J. Guldina. (*Z. anal. Chem.*, 1935, **101**, 406–413.)—The process, which is based upon the differential stability of the fluosilicate and fluoberyllate ions, embodies an earlier method for the determination of beryllium (ANALYST, 1934, **59**, 645).

(*a*) If the quantity of sodium fluosilicate present is small, the solution to be titrated (20 to 25 ml.) is treated with an equal volume of 20 per cent. calcium chloride solution, and the liquid is titrated with 0·5 *N* sodium hydroxide solution until neutral to methyl orange (1 ml. of the alkali ≡ 0·0075 g. SiO_2). The solution is then diluted to 200 or 250 ml., titrated against phenolphthalein to a pink end-point persisting for 30 seconds, heated to boiling, and titrated until the pink colour is permanent (1 ml. = 0·00625 g. BeO).

(*b*) If much sodium fluosilicate is present, the determination of silica is carried out in a separate portion as under (*a*). For the beryllia determination the solution (100 to 200 ml.) in a 250-ml. graduated flask is treated with 20 to 25 g. of potassium chloride, diluted to the mark, left for 20 minutes, and filtered. An aliquot part of the filtrate is treated with 20 to 25 ml. of 20 per cent. calcium chloride solution, and the remaining traces of sodium fluosilicate are titrated as above, methyl orange being used as indicator. The solution, diluted to 200 or 250 ml., is then titrated for beryllium as described under (*a*). W. R. S.

Precipitation of Titanium as Phosphate. T. Da-Tchang and L. Houong. (*Compt. rend.*, 1935, **200**, 2173–2175.)—Solutions of titanic chloride were precipitated with excess of diammonium phosphate at water-bath temperatures. The precipitate formed slowly, and the solution was left for 12 hours to clear. The precipitate was collected, washed by decantation with 5 per cent. ammonium nitrate solution first, then with water, dried, ignited, and weighed. Precipitation at increasing acidities showed that the ratio of titania to titanium phosphate remained constant at an acidity range of 1 to 10 per cent., the mean ratio being 0·5234. The formula $Ti_2P_2O_8$ requires a titania factor of 0·506, whilst that for $Ti_3(PO_4)_4$ is 0·458. The authors propose the empirical factor 0·5234. Complete precipitation of the titanium requires a molecular ratio of TiO_2:100 $(NH_4)_2HPO4$, and a minimum concentration of 10 per cent. of the precipitant. W. R. S.

Determination of Small Quantities of Boric Acid by a Flame-test. W. Stahl. (*Z. anal. Chem.*, 1935, **101**, 342–347; 348–356.)—Further details are given of the technique and apparatus previously described (Abst., ANALYST, 1931, **56**, 340) for the colorimetric flame-test as devised by the author. Test analyses and determinations of boric acid in sea-water are reproduced. The process detects 0·007 mg. of boric oxide, and the error is stated not to exceed 15 per cent.

W. R. S.

Detection of Ferricyanide in Presence of Ferrocyanide. I. M. Korenman. (*Z. anal. Chem.*, 1935, **101**, 417–419.)—Ferricyanide oxidises indigo carmine in alkaline solution to pale-yellow disulphodehydroindigo. The reaction is carried out as follows:—A test-tube contains 3 ml. of water, another tube 3 ml. of solution. Each tube is treated with 10 drops of saturated sodium carbonate solution, then with a few drops of 0·02 per cent. indigo carmine solution. The aqueous solution remains blue, whilst the colour is rapidly discharged by ferricyanide, if present in the unknown solution. If larger amounts are present, the blue colour is instantly discharged, no blank test being required. The sensitiveness is given as 1:600,000. Ferrocyanide, chloride, bromide, and thiocyanate do not interfere, but hydrogen peroxide must not be present. W. R. S.

Identification of Halides in presence of Thiocyanate. G. B. and L. K. Heisig. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 249–250.)—By the following method it was found possible to detect a minimum of 0·25 mg. of iodide ion, 0·5 mg. of bromide ion and 0·25 mg. of chloride ion in the presence of 100 mg. of thiocyanate ion. *Test for Iodide.*—To 10 ml. of neutral solution are added 1 ml. of carbon tetrachloride and 0·5 g. of potassium persulphate, and the liquid is shaken. A violet colour indicates iodine. *Removal of Iodide and Test for Bromide.*—The carbon tetrachloride layer is removed, and the solution is evaporated to dryness after being made alkaline with an excess of 15 ml. of 2 *N* sodium carbonate solution. The residue is dissolved in 10 ml. of water and tested for freedom from iodide by acidifying with nitric acid, adding 1 ml. of carbon tetrachloride and a few small crystals of potassium persulphate, and warming gently. A colourless liquid should result, but, if a large amount of iodide was originally present, the carbon tetrachloride layer may be coloured with iodine, in which case the liquid must be repeatedly extracted with carbon tetrachloride, with intervening additions of potassium persulphate, to remove the iodine. One ml. of carbon tetrachloride and 4 ml. of concentrated nitric acid are added to the cold solution contained in a white dish. The formation of a yellow colour, which persists after 1 minute with occasional stirring, indicates bromide. *Removal of Bromide and Test for Chloride.*—The bromide ion is removed, if present, by adding a slight excess of potassium permanganate and boiling for 1 minute. The sulphate formed by the decomposition of the potassium persulphate must now be removed by the addition of a slight excess of barium nitrate, as otherwise silver sulphate may separate in the next stage. The barium sulphate is filtered off, and the solution is tested for chloride by the addition of silver nitrate. S. G. C.

Rapid Method for Determining Hydrogen Sulphide in Gaseous Mixtures. P. Woog, R. Sigwalt and J. de Saint-Mais. (*Bull. Soc. Chim.*, 1935, **2**, 1214–1216.)—A rapid method for determining hydrogen sulphide in gaseous mixtures or in the atmosphere consists in exposing a suitable indicator paper in a given volume of the gas and comparing the colour developed with a scale. The paper is prepared by soaking bands of filter paper, 30 mm. by 8 mm., in a bath containing 10 g. of crystalline lead acetate, 50 ml. of water and 50 ml. of pure glycerin, and drying between filter paper. Prepared thus, the papers are stable, and retain sufficient moisture. They are quickly placed in glass tubes of about 15 ml. capacity, which are exhausted and sealed. When required, the point of the ampoule is broken in the gaseous mixture, which fills the ampoule, and the orifice is then closed with a wad of cotton wool, the ampoule shaken, and the colour of the test-paper compared with the scale of coloured papers. These are prepared by impregnating filter-paper with a 10 per cent. solution of lead acetate without glycerin, exposing the paper while still damp to air containing known quantities of hydrogen sulphide, and then drying. In this way proportions of hydrogen sulphide between 1 part in 300 and 1 part in about 20,000 may be determined approximately. The sensitiveness of the reaction may be increased to 1 in 80,000 by using smaller strips of filter-paper. D. G. H.

I. Colorimetric Determination of Phosphate. C. Zinzadze (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 227–230). **II. Colorimetric Determination of Arsenate in Phosphate-free Solution. C. Zinzadze** (*id.* p. 230.)—I. *Phosphate.*—Various modifications of the molybdenum-blue method are reviewed. A disadvantage of the use of sulphite alone as a reducing agent is that the liquid requires heating at 100° C. for 30 minutes for the full development of the blue colour. Stannous chloride, the reducing agent used by the originator of the molybdenum-blue method (Osmond, *Bull. Soc. Chim.*, 1887, **47**, 745), works in the cold, but whilst the colour produced is less stable than that formed by sulphite reduction, it is nevertheless not so subject to interference by arsenate, silica, iron, etc. The stability of colour is improved by the addition of gum arabic, as in the following revised method devised by the author. *Stannous Chloride Reduction.*—*Method* (*a*) [Suitable for determining 0·01 to 0·3 mg. of P_2O_5 in about 15 ml. of solution in presence of the following constituents up to the amount stated: arsenic pentoxide, 20 mg.; nitric acid, 50 mg.; ferric iron, 50 mg.; silica, 150 mg.]. The solution, contained in a 50-ml. graduated flask, is neutralised with dilute sulphuric acid or sodium bicarbonate solution, 5 drops of saturated aqueous 2:4-dinitrophenol solution being used as indicator (yellow colour at end-point); 5 ml. of *N* sulphuric acid and 5 ml. of sodium bisulphite solution (8 per cent. of anhydrous salt) are added, and the solution is kept overnight or heated on a steam-bath for 1 hour to effect preliminary reduction of arsenic.* Five ml. of cold molybdic oxide reagent (4·01 g. of pure MoO_3 dissolved by heating in 101 ml. of 25 *N* sulphuric acid and diluted to 1 litre) are added, followed by 5 ml. of stannous chloride and gum arabic solution (0·16 g. of pure $SnCl_2{\cdot}2H_2O$ in 200 ml. of 1 per cent. gum arabic solution). The liquid is diluted to 50 ml. and compared colorimetrically after 20 minutes with

[**Abstractor's Note.*—The reduction may not complete.]

a standard phosphate solution which has been treated in a similar manner at the same time as the test solution. A suitable standard phosphate solution contains 0·0767 g. of potassium dihydrogen phosphate, together with 10 ml. of *N* sulphuric acid and 6 drops of 0·1 *N* permanganate solution as preservatives, in 2 l.; 1 ml. ≡ 0·02 mg. of phosphorus pentoxide. *Method* (*b*).—When the solution to be tested contains not more than 2 mg. of ferric iron and 10 mg. of nitrate, method (*a*) can be shortened by omitting the addition of sulphuric acid and bisulphite between the stages of neutralising and adding the molybdic oxide reagent. Arsenate behaves like phosphate in method (*b*), and must, therefore, be absent when phosphate is determined. The necessity for high purity of reagents for the above methods is emphasised.

II.—*Arsenate.*—Arsenate (0·005 to 0·3 mg. of As_2O_5) may be determined like phosphate by the use of Method (*b*) (above); the restriction as to the permissible amounts of iron and nitrate which may be present is the same. A suitable standard arsenate solution may be prepared by dissolving 0·020 g. of pure arsenic pentoxide in 5 ml. of 2 per cent. sodium bicarbonate solution, adding 10 ml. of *N* sulphuric acid and 3 drops of 0·1 *N* permanganate solution as preservatives, and diluting to 1 l. 1 ml. ≡ 0·02 mg. of arsenic pentoxide. Method (*a*) (above) is not applicable, as the sulphite interferes. S. G. C.

Microchemical

Micro Detection of Magnesium and Aluminium with Alkannin and Naphthazarin. J. V. Dubský and E. Wagner. (*Mikrochem.*, 1935, **17**, 186–190.)—On the assumption that the colouring principle of alkanna tincture consisted of hydroxyanthraquinones, Hahn, Wolf and Jäger (Abst., ANALYST, 1925, **50**, 35) examined the reactions of a number of these compounds with magnesium salts. It was found that the reddish-violet alkaline solution of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone is changed to cornflower-blue by magnesium, this change forming a very sensitive means of detecting magnesium. It has recently been shown that alkannin is a naphthazarin derivative (5 : 8-dihydroxy-1 : 4-naphthaquinone), and the examination of the colour changes of alkannin and naphthazarin with magnesium (and aluminium, *cf.* Estill and Nugent, Abst., ANALYST, 1926, **51**, 161), now described, affords confirmatory evidence of this constitution.

Two procedures are given for the detection of magnesium. (1) To 5 ml. of the liquid under test are added 5 drops of either a 0·05 per cent. alcoholic solution of alkannin or a 0·03 per cent. naphthazarin solution and, dropwise, rather more 2·5 *N* sodium hydroxide than suffices to produce the colour-change. Either immediately, or on heating, a cornflower-blue precipitate forms with as little as 0·05 mg. of magnesium. A control test with water is also made. (2) To a few drops of the liquid are added a few drops of a mixture of 5 ml. of 0·03 per cent. naphthazarin solution and 1 ml. of 4 per cent. ethylenediamine solution, the whole being then heated gently. A blank test is also made. A blue colour forms in presence of 0·35γ or more of magnesium, the limiting concentration being 1 in 66,000. In Estill and Nugent's test for aluminium the alkannin used may be replaced by naphthazarin. T. H. P.

Quantitative Drop Analysis. III. The Kjeldahl Nitrogen Determination and Determination of non-protein Nitrogen of Blood. P. L. Kirk. (*Mikrochem.*, 1935, **16**, 13–24.)—The method is used for the determination of amounts of nitrogen varying from 4 to 16γ, with a mean error of about 1 per cent. and a maximum error about 3 per cent. The apparatus and technique of the titration part of the determination are the same as previously described (*Mikrochem.*, 1933–34, **14**, 1, 15; Abst., ANALYST, 1934, **59**, 63, 64). The distillation apparatus is somewhat similar in design to the Parnas and Wagner apparatus, but reduced in size; it can easily be made in the laboratory. Compressed air, the pressure of which is adjusted by means of a simple water-pressure regulator (as used in the Pregl carbon and hydrogen determination), is passed through the steam generator, which has a capacity of 50 ml., and is heated by an ordinary micro-burner. The steam-trap is 10 cm. long and 1·5 cm. in diameter, with the usual rubber outlet tube and clip at the bottom for drainage; the top exit is made from tubing 4 mm. in outer diameter which passes through a rubber stopper fitted into the filling funnel which is an integral part of the distillation flask. The distillation flask has a boiling-chamber of 5 ml. capacity. The condenser is made from 4 mm. tubing and sealed into the trap of the distillation flask by means of a ring-seal; it is cooled by means of several layers of moist filter-paper. The condenser tube terminates in a small bulb connected through a ring seal with the bottom of the receiver, which consists of a tube 4 cm. long and 1 cm. in diameter, on which is a bulb 1·2 cm. in diameter. During the actual distillation, air is passed through into the steam generator at the rate of 3 bubbles in 2 seconds. The total volume in the distillation flask should not exceed 2·5 ml., including the digest water, 5 or 6 drops of alcohol, and the calculated amount of strong alkali to neutralise the acid used in the digestion. The distillation flask is gently heated (not to boiling) for 2 or 3 minutes, and the temperature is then raised until the contents boil, and a distillate of 0·2 or 0·3 ml. has been obtained; further distillation tends to obscure the end-point in the titration. During the titration the distilling flask-condenser receiver is disconnected, and a small medicine dropper (or fountain-pen filler) is inserted through the filling funnel of the distillation bulb, and by squeezing the bulb of the dropper, stirring is effected. With pure reagents a blank of not more than 0·5λ of 0·05 *N* solution is obtained. The digestion is carried out in small Kjeldahl flasks, with bulb diameter of 2 cm.; a capillary outlet tube is drawn out of the bulb to facilitate washing and transference of the contents. About 0·1 ml. of concentrated sulphuric acid is used for each sample, and, if necessary, after 5 minutes' digestion, 15λ of perhydrol or superoxol, diluted with 2 volumes of water, are added to complete the decomposition. The method was tested on a number of pure compounds.

J. W. M.

Apparatus

Apparatus for the Quantitative Recovery of Dialysates. P. Loch. (*Z. anal. Chem.*, 1935, **101**, 385–388.)—The raised rectangular vessel in which the dialysis is performed discharges by means of a constant-level syphon into a conical flask provided with a three-holed stopper, carrying (1) a tube reaching almost to the bottom of the flask, the upper end of which has a small funnel for receiving the discharge of the syphon; (2) an ascending tube cut off near the under-surface of the stopper, curved down at its upper end and connected with a descending Liebig condenser discharging into the dialyser; and (3) a syphon closed with a screw-clamp for sampling and emptying the contents of the conical flask. The latter stands on a tripod and is heated by a Bunsen burner. The dialyser being filled with water to the required level, a quantity of water is made to boil in the flask, distilling into the dialyser, which continuously discharges an equivalent amount of water through the syphon into the flask. W. R. S.

Reviews

TAYLOR'S PRINCIPLES AND PRACTICE OF MEDICAL JURISPRUDENCE. Ninth Edition. Edited by SYDNEY SMITH, M.D., F.R.C.P., and W. G. H. COOK, LL.D. In two volumes. Pp. viii + 878 and 973. London: J. & A. Churchill, Ltd. Price 63s.

The two volumes under review represent the ninth edition of this well-known work, the present edition and the previous one having been undertaken by Prof. Smith and Dr. Cook. In the preface they pay a tribute to Dr. C. P. Stewart for his assistance in the section on toxicology.

This book has rightly become the standard British text-book on medical jurisprudence, and it is to these volumes that the lawyer, the medical man and the chemist turn when a medico-legal problem presents itself.

It is therefore necessary that the most meticulous accuracy should be the aim of the editors, for their responsibility in presenting the work is great. For this reason it is pleasing to see that blunders of a previous editor have now been eliminated, and that most of the bad features of these editions are now a thing of the past. It is, for example, pleasing to see that such nonsense as the preparation of haemoglobin crystals from a suspected bloodstain and the examination of the nature of the crystals so produced is no longer advocated as a means of determining the source of the blood.

As this review is written for a journal devoted primarily to the study of analytical chemistry, it is only natural that the reviewer should pay his chief attention to the second volume, which deals with toxicology, but it is not possible to pass over p. 379 of Vol. I without some comment. On this page there appears to be a serious inconsistency which has remained uncorrected from the edition of 1920. It is best dealt with by actual quotation: "In most suicidal wounds which affect the throat the direction of the cut is commonly from left to right" (in right-handed persons). Lower down in the same paragraph we find "If (the assailant is) in front of the person whom he attacks, the direction would probably be from left to right; but in suicides, when the right hand is commonly used, it is the reverse." Here is an obvious contradiction in the same paragraph, which should be rectified.

In these days, when space in books is so valuable, it does seem a little unnecessary, in a scientific work of this kind, that mention should be made of—much less some five or six pages devoted to—spontaneous or preternatural combustibility of the human body.

The section on blood makes mention of the blood-groups, and reference is made to their utilisation in examining a bloodstain. As this test has now become part of the routine examination of bloodstains, it would be desirable for a fuller account of the technical details to be given, especially regarding the vital part of the test, namely, the controls.

In the paternity section no mention is made of the M and N sub-groups or reference made to the work of Thomsen and others on them. The utilisation of the M and N groups increases immeasurably the chances of coming to a decision in a particular case, and their use has now become a routine procedure in many continental countries. It is, too, specially desirable that a full account of these tests and their practical application should be given, for it is time that the judicial authorities of this country realised the assistance that can be given to them in what has often been stated to be the most difficult class of case which a bench of magistrates is called upon to decide, and a class of case where miscarriages of justice are not unknown.

Turning now to Volume II, the reviewer proposes to deal mainly with the toxicological section, and if, in so doing, he offers certain criticisms, it is to be understood that these are made in no carping spirit, but solely with a sincere desire to enhance the utility of this important section.

1. It is a matter of opinion, and no opinion is offered here, whether works of this type on toxicology should contain analytical details of methods of test and determination of the poisonous substances in the cadaver which are referred to in the text; but, if these are to be included, it is useless to give a brief summary of methods. Full working details must always be given.

2. The arts of medicine, pathology and analytical chemistry have advanced immeasurably in the last few decades; consequently, the editors may with advantage consider very carefully whether many of the older cases quoted would not better be now omitted in favour of more recent ones. In dealing with the footnote references at the bottom of about 200 consecutive pages we find that approximately:

7 per cent. of these references are dated 1800–1849
37 „ „ „ „ „ „ „ 1850–1874
17 „ „ „ „ „ „ „ 1875–1899
22 „ „ „ „ „ „ „ 1900–1924
17 „ „ „ „ „ „ „ 1925–1934

Certain of the older cases quoted may be the only cases available, and so may be left, and others no doubt belong to the *cause célèbre* group,—but even here they may be misleading, in view of modern knowledge on the subject. But the majority of the earlier ones may well be omitted in favour of more recent cases. The reviewer has had occasion to look up old references from time to time, and, in certain instances, reading of the original papers has left no doubt in his mind that there is now no scientific interest in quoting the case to-day.

3. In some of the older cases, details are scanty, post-mortem examinations were unsatisfactory, and no analysis was made. Such cases, unless there is abundant proof that the poison was taken (not merely the uncorroborated word of the patient

to the medical attendant), would be far better omitted in a work the reputation of which it is so important to preserve.

4. Coming now to the space devoted to individual poisons, it is not necessarily an axiom that the space must be directly proportionate to the frequency of the poison, but it might be a reasonable working basis. Yet lysol, the second most commonly-used poison to-day, receives a scanty mention of some 2 pages, and no reference to cases is later than 1900. Statistics quoted from a book published in America in 1911 do not materially assist, and the symptomatology has to be deduced from the cases quoted. The condition of the urine, the after-effects in recovered cases, the post-mortem appearance, and the analytical details, are amongst the matters lacking.

It is not the intention of the reviewer to pursue this matter further; enough has been said to indicate the necessity for full revision, and it cannot be reiterated too strongly that it has been said in a most sincere desire to help. Such a revision will be no light task, but one well worthy of a book which has been in existence since 1843, and which will soon have the privilege, not accorded to many scientific works, of celebrating its centenary. Perhaps it will not be too much to hope for, that this revision will be complete by that time, and be worthy of those early editions prepared by Taylor and Stevenson.

It is appreciated that much valuable material—such as might be included in this work—is not available owing to lack of publication, but I feel sure that the editors will, if they ask, receive generous assistance from the private notes of pathologists and analysts, for it is in the interest of all to see that such a work is comprehensive and accurate.

The reviewer is mindful of the great amount of work that the editors must have given to this edition, and desires to tender to them his appreciation of it. A tribute may rightly be paid to the proof-reading and freedom from errors from this cause, and to the publishers, who have maintained the general standard of make-up and binding of the volumes.

G. ROCHE LYNCH

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. Supplement, Vol. II. N–Z. Edited by J. F. THORPE, D.Sc., F.R.S. and M. A. WHITELEY, D.Sc. Pp. 727. London: Longmans, Green & Co. 1935. Price 60s.

Apart from the index,* "Thorpe" is now complete and up-to-date once more; the encyclopaedic character of this guide to the complexities of modern chemistry recalls a line from Pope:

> *"A mighty maze! but not without a plan."*

It is the skill of the editors, as well as the ability of the many contributors, which has earned for "Thorpe" a unique place on the shelves of English chemists, and this last volume worthily maintains the family tradition. The new articles are not only authoritative but thoroughly up-to-date. Pure theory is skilfully interwoven with practice, both in the articles and in their selection. Thus, for example, Dunstan, on the technical developments of petroleum, follows Sugden, on the theoretical implications of the parachor. Linstead writes on the new phenols and their derivatives, while Baly contributes a section on photosynthesis which is truly of "absorbing" interest; if photosynthesis is still theoretical to us, it is most certainly the "applied chemistry" of nature. Then, if we read on, we come to earth again in an article by Tattersfield on plant sprays and insecticides. So one might go on describing some of the major new articles; but, perhaps, this is not the way to read a dictionary which is, after all, a reference work. Its real value lies not so much in exhaustive discourses on any particular topic as in the excellence and multiplicity of minor paragraphs and references; these very often give just that item of information which the technical chemist needs, and, if the particular item of information is not there, there is usually a reference to original literature which supplies the need. In this connection commendation may be expressed for the thoroughness with which new topics have been surveyed, such, for example, as synthetic resins (Morrell), wetting-out agents (Clayton), oil from coal (Lander), new synthetic drugs (Stedman), and vitamins (Harris).

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* It has been found necessary to reserve the index and a glossary of new terms and phrases for issue as a further small volume later in the year.

If a criticism is to be put forward it must be with diffidence, for the proper allocation of space must be unconsciously coloured by one's point of view; perhaps rather much space is devoted to certain articles on theoretical topics on which information is usually sought in the specialised monographs. If space is to be conserved, it should be at the expense of "pure" chemistry in a dictionary of "applied" chemistry.

Considering the two volumes of the supplement together, they are excellent; the style and format leave nothing to be desired; they are accurate, so far as can be tested in a short period of use or in reviewing, and remarkably free from errors, typographical or otherwise. The dictionary is worthy of pride of place on our shelves, and no one who has had occasion to use it could afford to be without it, or even to be without the supplement, and we would congratulate the editors on the successful completion of a work which is a reliable guide in the maze of modern chemistry.

H. E. Cox

AIDS TO THE ANALYSIS OF FOODS AND DRUGS. By C. G. MOOR and W. PARTRIDGE. Fifth Edition. Revised and partly rewritten by J. R. NICHOLLS. Pp. viii+322. London: Baillière, Tindall & Cox. 1934. Price 5s.

Perusal of the new edition of this excellent little manual revised by Mr. Nicholls was anticipated with many expectations, which have, on the whole, been realised. In the previous edition—now 17 years old—many of the data are necessarily obsolete, and the keynote of this review must be praise to the reviser for the thorough manner in which he has succeeded in bringing information up-to-date and in adding useful pertinent matter.

The generous scattering of recent references; the incorporation of legal standards at present operating; the new monographs on preserved and foreign eggs, preservatives and prohibited colours; very useful and up-to-date information on the determination of poisonous metals and useful tables of comparison of starches, considerably enhance the value of this new edition. A scheme for the analysis of unknown drugs is also included. A little information on flesh foods would have made the meal more complete.

Most sections have been partly rewritten, that on sugar being almost entirely new. The revision of the monographs on milk and butter is praiseworthy. Clearer subheadings have facilitated reference, and the text is unusually free from error.

If there are to be, as we hope, further editions of this work, Mr. Nicholls might well revise the style of the original authors; such an expression as "an excess beyond the iodine put out of action by oil is required to bring off the test" (p. 149) should not be difficult to improve.

The section on drugs, in comparison with the food section, is a little disappointing, as the strides made since the earlier edition and the need for assistance in this field have been sufficient to lead us to hope that this section would be more helpful. Much of the available space might have been devoted to the pressing problem of those drugs and galenicals the analysis of which is not included in the Pharmacopoeia.

One almost becomes intoxicated by the mass of information on alcohol and alcoholic-strength determination, much of which is superfluous, as no analyst would undertake drug work without the Pharmacopoeia at hand, where all this can be found; and to devote one-third of the total drug section to alcohol is out of proportion to the space accorded to the remaining subjects.

A monograph on such a complex subject as the analysis of unknown drugs is somewhat pretentious for a book of this size, and one feels that the well-known Stas-Otto process, tempered with a little chemical perception, would reach the same objective as that achieved by the proposed method. The inclusion of the alkaloidal reactions in tabulated form, however, is convenient and useful.

The value of the book lies in the inclusion of complete analytical details, enabling methods to be followed without further reference to original papers. Its size and cheapness should not discourage the analyst and student desirous of purchasing a really useful book, and they would do well to have such a mine of information constantly available.

D. C. GARRATT

METALLURGY. AN ELEMENTARY TEXT-BOOK. By E. L. RHEAD, M.Sc.Tech., F.I.C., A.I.M.E. New Edition. Pp. xiv+382. London: Longmans, Green & Co. 1935. Price 10s. 6d.

A review of the preceding edition of this well-known text-book appeared in Vol. L of the ANALYST, 1925, 207. The new edition is a slightly enlarged reproduction of the last, the plan of the book and the sequence of the text-matter remaining unaltered. Three new sections—on pyrometry, metallography, and foundrywork—have been added. New paragraphs and illustrations have been inserted in other sections, *e.g.* on physical tests, fuel, electric furnaces, hydrometallurgical processes.

Apart from the above additions, the book is substantially a re-impression of the preceding one; hence there is little the reviewer can usefully add to his former remarks and criticisms. In this "New Revised and Enlarged Edition" the size has been increased from crown 8vo to demy 8vo, the type setting is closer (8 lines per inch against 7), and there is a decrease of 21 in the number of pages; unfortunately for the student, these changes involve an increase in price of three shillings. Although the type must have been entirely re-set, the minor inaccuracies and peculiarities of style noticed in the last review have been faithfully reproduced in this edition. Thus, platinum is still found associated with rubidium (p. 333). Further instances of poor proof-reading are: H_2SiF_4 and $PbSiF_4$ for hydrofluosilicic acid and its lead salt (p. 257); Cotterill (p. 257) and Cottrill (p. 285) for Cottrell; malleablising (p. 350) and malleabilising (p. 361); cerusite (p. 240).

As an elementary treatise adequately dealing with general principles, and more particularly the metallurgy of iron and steel, this work will no doubt continue to enjoy the popularity to which it is entitled.

W. R. SCHOELLER

VAN NOSTRAND'S CHEMICAL ANNUAL. Edited by JOHN C. OLSEN, A.M., Ph.D., D.Sc. Seventh Issue. Pp. xvii + 1029. London: Chapman & Hall, Ltd. 1935. Price 25s. net.

This volume would appear very successfully to fulfil the function described in the sub-title, namely, that of a handbook of data useful to analytical, manufacturing and investigating chemists, chemical engineers, and students. It does not attempt to deal in detail with laboratory methods, for which the appropriate text-books may be more suitably consulted, but presents a vast amount of chemical and physical data of general utility, together with information of a more specialised character necessary for those engaged in chemical manufacture.

The requirements of the analyst are not, however, neglected, and tables of the physical constants of over 2250 inorganic and 3070 organic compounds are given, the data, within the scope of the table, being gratifyingly complete. For example, the temperature ranges of stability of the various hydrates of metallic salts are given; it is frequently helpful to know just how much water of crystallisation is lost, say, at 100° C.

The book is up to date in giving adequate space for tables appertaining to modern physico-chemical methods. It may be of interest to note that the immersion refractometer method for the determination of mixtures of methyl and ethyl alcohols in aqueous distillates is dealt with, and a useful graph is provided for the conversion of the Saybolt and Redwood constants to units of absolute viscosity. The general utility of the alcohol specific gravity table on p. 634 *et seq.* is somewhat limited, in that no figures are given for solutions of strength exceeding 50 per cent. by volume; incidentally, there is a very slight variation throughout from the tables issued by H.M. Customs and Excise.

The physical and chemical constants of a very comprehensive list of oils, fats and waxes are given, and a list of reaction equations for volumetric computations is a notable feature. Some sixty pages at the end of the volume are devoted to a bibliography of the more important technical books which have appeared since 1925, comprising American, English, French, Italian and German publications.

J. U. LEWIN

OCTOBER, 1935 Vol. 60, No. 715

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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Obituary

CHARLES THOMAS KINGZETT

To most of our members Kingzett had become little more than a name, but in his early days he took a prominent part in the organisation of the profession of chemistry, being one of the original members of the Institute of Chemistry when it was founded in 1877.

He was born in 1852 at Oxford, was educated there, studying chemistry under Sir Benjamin Brodie, and began his professional career as assistant to Madan at the University Laboratory. Afterwards, for a short time, he was science master in a school, but in 1870 abandoned teaching in favour of technical chemistry, becoming chemist to the Liverpool Soda Works. Soon afterwards he went as research assistant to Thudichum, with whom he remained for some years, until, in 1877, he started a consulting practice in partnership with Dr. B. H. Paul.

An investigation of the antiseptic properties of conifer essential oils had a commercial result in the establishment of the Sanitas Company, Ltd., of which Kingzett was first chemist and technical manager and afterwards chairman.

He was one of the oldest surviving members of our Society, which he joined in 1881, becoming Vice-President in 1885. Several papers were contributed by him to early issues of THE ANALYST, including "Analyses of Asphalte Pavements" (1882, **7**, 4) and "The Estimation of Hydrogen Peroxide" (1888, **13**, 62), and his last communication, on "The Absorption of Oxygen by Phosphorus," was published last year (ANALYST, 1934, **59**, 816).

Of recent years Kingzett's name became familiar to the general public by the publication of successive editions of his *Chemical Encyclopaedia*, the fifth edition of which appeared in 1932, and was reviewed in our journal (ANALYST, 1932, **57**, 809). This last edition showed that the author had kept a receptive mind to modern advances in chemical theory. Another semi-popular book was a collection of essays, first published in 1880 under the title of "Nature's Hygiene"; it ran through several editions, the fourth of which was reviewed in 1898 (ANALYST, **23**, 191).

Kingzett died on July 29th at his home at West Byfleet, and the Society was represented at his funeral by Mr. R. L. Collett.

EDITOR

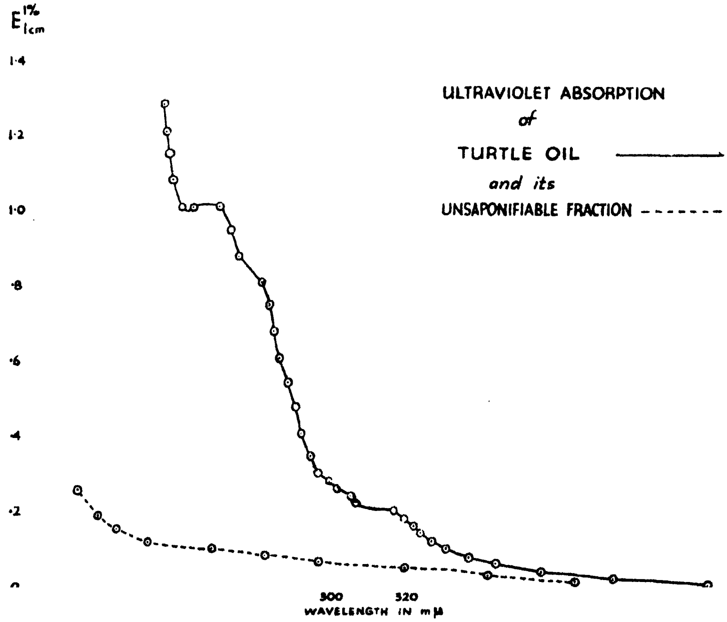
The Physical and Chemical Characteristics of Turtle Oil

By WALTER LEE, A.I.C.

(Work done under the Society's Analytical Investigation Scheme)

INTRODUCTORY.—In the *Pharmaceutical Journal* (1934, **132**, 592) attention is drawn to the recent use of turtle oil in cosmetic preparations. It is claimed that the oil is very easily absorbed by the skin, and that, although some skins react to it unfavourably, as its action is supposed to be markedly astringent, it could form the basis of an ideal "skin-food." The women of Indian tribes in Mexico, who use turtle oil extensively for this purpose, are notably free from wrinkles, even the older women. Its use for this purpose has, however, been restricted in the past by the very objectionable odour of the crude oil, but refined oils have recently been placed on the market for use in cosmetics, and these have only a faint odour easily masked by appropriate perfuming. The refined products vary from light yellow semi-fluid oils to golden-yellow oils of butter-like consistence.

SOURCES AND VARIETIES.—Most of the commercial oil is obtained from the muscles and genital glands of the giant sea-turtle, the turtles used being from 250 to 700 years of age and weighing from 300 lbs. There are several varieties of the oil on sale in England, but only one has any real market, and most of the experimental work here described was done on this type of oil. A specially "processed" and deodorised oil is also on sale, but principally in South Africa. This is very light in colour, whereas an Egyptian oil, which has a greater sale in



this country and is supposed to be obtained from the liver and glands, is of a much deeper yellow colour. I have been unable to discover the habitat of the turtles from which the Egyptian oil is obtained, but it is known to be different from that of the oil mainly used in this work; this oil comes from an isolated district on the west coast of Africa.

EXPERIMENTAL.—Four separate pounds of the refined West African oil, as purchased, were mixed in a dry container. The product was solid at ordinary room temperature and light yellow, had a mild but quite distinct odour, and melted to a golden-yellow oil. It bleached on exposure to light.

The following values were determined on the filtered oil:

Melting-point (incipient fusion)	24·6° C.
,, (final fusion)	25·6° C.
Solidifying-point	22·5° C.
Titre	25·5° C.
Sp.gr. at 40°/40° C.	0·9112
Refractive index, n_D^{40}	1·4599
Saponification value	209
Unsaponifiable matter (S.P.A. method)	0·6 per cent.
Iodine value of the unsaponifiable matter (Bolton and Williams method)	92·5
Iodine value	64·6
Acid value	2·0
Percentage of insoluble bromides on the free acids (Gemmel's method)	5·0
Melting-point of the bromides	darken above 200° C.
Reichert–Meissl value	0·2
Polenske value	1·7
Kirschner value	0·06
Acetyl value	3·5

Small quantities of the three varieties of oil mentioned (6–10 g.) were obtained, and these gave the following values:

Type of oil	n_D^{40}	Iodine value	Saponification value	Unsaponifiable matter (petroleum spirit extraction) Per Cent.
(1) Specially "processed" and deodorised oil	1·4599	66·6	214·0	0·44
(2) Egyptian oil	1·4585	57·2	213·5	0·30
(3) African oil (same source as that of main bulk)	1·4599	67·8	209·0	0·43

The Egyptian oil has, therefore, a lower state of unsaturation and a lower content of unsaponifiable matter.

The oil was stated to be particularly rich in vitamins, and this was supposed to be one of the contributory factors towards its astringent action. Dr. Lester Smith has measured the ultra-violet absorption spectrum, using a Spekker photometer and a Hilger E2 spectrograph. The oil was examined in ethereal solution at concentrations of 5 per cent. and 1·5 per cent. in a 1-cm. cell. The intensities of absorption, expressed as $E^{1\%}_{1\,\mathrm{cm.}}$, are shown in Fig. 1. A sample of the oil was saponified by boiling for a few minutes with alcoholic potash, and the unsaponifiable matter was exhaustively extracted with ether. The solution was made up to a strength corresponding with a 5·83 per cent. solution of the original oil, and the absorption spectrum of this solution was measured in a 1-cm. cell. The absorptions, calculated to $E^{1\%}_{1\,\text{cm.}}$, are shown in the same figure (the concentration is that of the equivalent amount of oil, not that of the unsaponifiable fraction itself).

It is clear, from inspection of the two curves, that the bulk of the absorption of the turtle oil is due to the glyceride fraction, since the absorption is so greatly diminished when the unsaponifiable fraction freed from glycerides is examined. The very low intensity of absorption of the unsaponifiable fraction and the absence of any inflections in the curve indicate that no significant amounts of vitamin *A*, ergosterol or other pro-vitamin *D* are present, and also point to the absence of vitamin *E*.

COLOUR TESTS.—The sulphuric acid liver-oil test was completely masked, although as this variety of oil is not supposed to be a liver oil, no positive result was expected. Halphen's cottonseed oil test, the furfural sesamé oil test, and, in view of the close resemblance of some of the values to those of lard, crystallisation from ether were all tried. In no case did any characteristic colour or form develop.

REMARKS.—Several analyses of turtle oil are recorded by Lewkowitsch (*Technology of Oils, Fats and Waxes*, 6th Ed., Vol. II, p. 475), and the figures were compared with those obtained with the refined oil. As was to be expected, appreciable differences were found in all those figures that might conceivably be altered by modern refining processes. The following table illustrates this:

Observers	Zdarek	Sage	Tsujimoto	Lee
Sp.gr.	0·9198 at 42·5° C.	0·9192 at 25° C.	0·9335 at 15° C.	0·9112 at 40° C.
Solidifying-point	10–0	19–18	—	22·5
Melting-point	23–27	24–25	—	24·6–25·6
Saponification value	209	211·3	193·8	209
Iodine value	112	111	127·4	64·6
Reichert–Meissl value	4·6	4·8	—	0·2
Refractive index	1·4677 at 30° C.	1·4665 at 50° C.	1·4769 at 20° C.	1·4599 at 40° C.
Insoluble bromide value, per cent.	29·45	—	—	5·0
Titre	28·2	—	—	25·5

It will be seen that the iodine value of the refined oil is about half that of the crude oil, whilst the insoluble bromide value, as might be expected from the greater saturation indicated by the iodine value, is also very much less. An insoluble bromide value of only 3·53 per cent. has, however, been obtained by Tsujimoto with snapping turtle oil. In that case the proportion of bromine in the bromo-acids did not correspond with the amount required for clupanodonic acid. The m.p. of the insoluble bromides from the oil I have examined shows that turtle oil is normal in this respect, which would not have been expected if the results obtained by Tsujimoto with snapping turtle oil had applied to this oil. Further features of the oil are:—(*a*) Its low content of unsaponifiable matter, (*b*) a Bolton-Williams figure falling within the range (90 to 96) given for this type of oil, and (*c*) a very low vitamin-content. It is also interesting to note that the unsaponifiable matter extracted by the S.P.A. method was regularly 0·1 to 0·15 per cent. higher than that obtained by a petroleum spirit extraction. Lastly, the refined oil has lost one of its characteristic features in having an almost negligible Reichert-Meissl value, against a value of nearly 5 given by the crude oil.

I wish to record my indebtedness to Mr. Manley for facilities for doing this work, to Mr. Houlbrooke for advice, and to Dr. Smith for the measurement and interpretation of the ultra-violet absorption spectrum.

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The Determination of Diacetyl and Acetyl Methyl Carbinol

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Various workers have determined diacetyl in butter, and, as the samples have been derived from different sources and the methods of analysis are not identical, it was not to be expected that the results would be uniform. The higher amounts are from highly flavoured butters, and there are wide variations in figures reported: 2 to 4 p.p.m. (van Niel *et al.*)[1]; 0·05 to 0·35 p.p.m. (Schmalfuss and Barthmeyer)[2]: 0·05 to 0·5 p.p.m. (Davies)[3]; and 3 p.p.m. (Testoni and Ciusa).[4]

The published methods for determining diacetyl and its precursor (hereinafter referred to as "carbinol") are all based on (*a*) separation of the diacetyl by distillation, and (*b*) precipitation of the diacetyl in the distillate as nickel dimethylglyoxime. Schmalfuss and Barthmeyer[5] and Michaelian, Farmer and Hammer[6] recommend the oxidation of the carbinol to diacetyl by means of ferric chloride, and the determination of this diacetyl with that already present in the sample. Another portion is distilled in an inert atmosphere of carbon dioxide for determination of the actual diacetyl-content. Davies[3] uses oleic acid as oxidising agent, and claims accurate yields (±3 per cent.) for small quantities of diacetyl obtained from butter. In general, the term "diacetyl" is loosely applied in the literature to both diacetyl and diacetyl plus carbinol. As none of the published methods so far examined gave satisfactory results, detailed experiments were made, and a modification was devised which gives consistent results, although with quantities ranging from 0·1 to 10 mg. they still tend to be slightly low.

Experimental

I. Conditions affecting the Completeness of Precipitation of Diacetyl as Nickel Dimethylglyoxime.—Most workers have followed van Niel's technique,[7] in which the dilute diacetyl solution is heated with the appropriate reagents for 1 hour at 80 to 90° C., and then cooled and allowed to stand for 24 hours before filtering and weighing. The experimental losses recorded by van Niel are, however, of the order of the actual amounts of precipitate commonly found from 1 kg. of butter. It was further observed that the residual filtrates deposited more precipitate when further heated. The conditions governing complete precipitation were therefore studied. Polak's "50 per cent. Diacetyl" (50·2 per cent. by actual determination) was freshly diluted when required as a standard; it is more stable than the pure chemical.

(i) *Reagents.*—A satisfactory mixture is: 4 ml. of 20 per cent. (w/v) hydroxylamine hydrochloride; 4 ml. of 20 per cent. sodium acetate solution; 2 ml. of 5 per cent. nickel chloride solution (free from cobalt and iron). Actually, a reagent of this composition recovered from previous determinations is preferable, particularly for the determination of the smaller amounts (see Part V).

(ii) *The Effect of the Period of Heating.*—(*a*) In experiments in which van Niel's conditions were followed (1 hour at 80 to 90° C. and 24 hours' standing) the following results were obtained:

Diacetyl taken mg.	Equivalent to nickel dimethylglyoxime mg.	Nickel dimethylglyoxime found mg.	Number of determinations	Error mg.	Error Per Cent.
0·20	0·34	0·30	2	0·04	—11*
2·00	3·4	3·0–3·1	7	0·3 to 0·4	—10
4·00	6·7	6·1	2	0·6	—9

* Determined colorimetrically by the method described later.

The incomplete precipitation was confirmed by the fact that, after further heating and cooling of the filtrates, the red nickel compound appeared.

(*b*) Experiments were then made with dimethylglyoxime (0·5 to 2·0 mg.) and the usual reagents. Precipitation was found to be complete, even after momentary heating to 90° C.

(*c*) The heating period for the actual diacetyl determination was extended to several hours on the hot-plate at 80 to 90° C. (during which it was allowed to evaporate), followed by overnight heating in a water-oven at 70 to 80° C. Within a small experimental error, which was inconsistent, the results were accurate, and, on evaporation of the mixed filtrates, only negligible amounts of the red nickel compound were detected. The results were as follows:

Diacetyl taken mg.	Equivalent to nickel dimethylglyoxime mg.	Nickel dimethylglyoxime found mg.	Number of determinations	Error mg.	Error Per Cent.
0·20	0·34	0·34	2	nil	—*
0·40	0·7	0·6–0·7	2	nil—0·1	—7
0·70	1·2	1·2	1	nil	—
1·00	1·7	1·6–1·7	6	nil—0·1	—3
2·00	3·4	3·4–3·5	4	nil—0·1	+2
5·00	8·4	8·5–8·7	2	+0·1–0·3	+2
10·00	16·8	16·9–17·2	3	+0·1–0·4	+2

* Determined colorimetrically by the method described later.

The conversion of diacetyl into the nickel salt of dimethylglyoxime takes place in the following stages:

(1) $CH_3.CO.CO.CH_3 + H_2NOH \rightarrow CH_3.C(:NOH).CO.CH_3 + H_2O$ (monoxime).

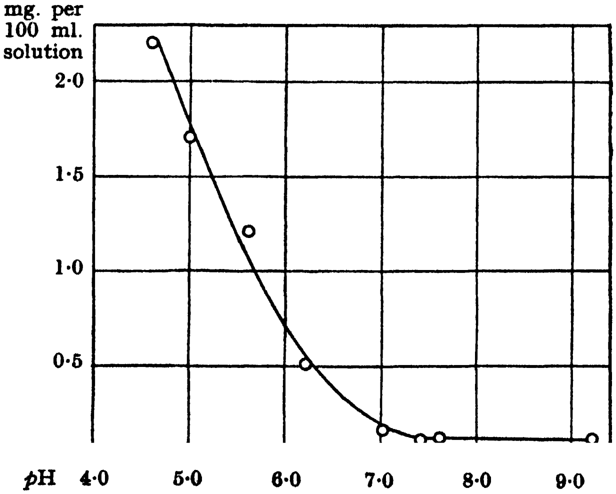
(2) $CH_3.C(:NOH).CO.CH_3 + H_2NOH \rightarrow CH_3.C(:NOH).C(:NOH).CH_3 + H_2O$
dioxime (dimethylglyoxime).

(3) $2CH_3.C(:NOH).C(:NOH).CH_3 + NiCl_2 \rightarrow [CH_3.C(:NOH).C:(NO).CH_3]_2Ni + 2HCl$.
Nickel diacetyldioxime (dimethylglyoxime).

Judging by the rapid disappearance of the odour of diacetyl when it is added in dilute solution to the hydroxylamine-nickel reagent, reaction (i) is rapid, whilst reaction (iii) is rapid when the solution is heated. It is therefore apparent that reaction (ii) is slow (being "non-ionic"), and requires prolonged heating for its completion, owing probably to steric hindrance at the vicinal carbonyl oxygen atoms when the combination with the second hydroxylamine molecule to form the dioxime takes place.

(iii) *The Effect of pH of Solution.*—The solubility of nickel dimethylglyoxime (previously dried at 110° C.) in dilute buffered sodium acetate solution is given in the following graph:

The reagent becomes acid on heating, and appreciable losses may occur unless ammonia is added to the solution after cooling, until the odour persists and the reaction is slightly alkaline to litmus paper. If ammonia is added before the original solution is heated, precipitation of nickel salts is likely to occur, leading to high results in the determination.



Solubility of nickel dimethylglyoxime in buffered sodium acetate (8 per cent.) solution

(iv) *The Period of Standing.*—Slight losses occur unless the nickel compound is given adequate time to crystallise after cooling and neutralisation of the solution, particularly when minute amounts are being determined. Three days appear to be sufficient, but it is safer to allow a considerably longer period of standing.

(v) *The Effect of Volume of Solution.*—In large volumes of solution (50 to 100 ml.) the losses slightly exceed the solubility losses, as shown in the graph, which is probably due to the incomplete conversion of the monoxime into the dioxime at high dilutions. It is therefore preferable, particularly when determining traces by the colorimetric method, to evaporate the solution (at 80 to 90° C.) for some hours on a hot-plate to a volume of 10 ml., by which means one avoids (*a*) the precipitation of nickel salts on adding ammonia, which is likely to occur if an excess of ammonia is inadvertently added, and (*b*) solubility losses.

II. THE SEPARATION OF CARBINOL + DIACETYL ("TOTAL DIACETYL") FROM BUTTER BY DISTILLATION.—For the determination of "total diacetyl" the carbinol is oxidised during distillation to diacetyl, which is estimated together with that already present.

(i) *Apparatus and Method.*—Glassware with ground-glass joints is desirable, but may be replaced by stock apparatus with rubber bungs which have been roughened with sandpaper, treated with several coatings of "Durofix" adhesive (a cellulose preparation), and dried after each application in a water-oven. This coating only occasionally needs patching or renewal. A bolt-head round-bottomed flask is used for the distillation, and its capacity must be rather more than twice the total volume of the butter and oxidising solution. The inlet tube from the steam-generator ends in a small bulb bored with several holes, by which means the entering jets of steam promote the mixing of the melted butter-fat with the underlying (oxidising) solution. The still-head is a wide glass tube with a bulb, and must be heavily lagged.

The underlying solution is $N/10$ with respect to sulphuric acid, and sufficient solid sodium chloride to saturate the solution and the butter serum is weighed into the flask after the butter sample. A 50-cm. Liebig condenser carries an adapter which *dips into the hydroxylamine-nickel reagent*, and the distillate is stirred into the reagent at short intervals. The condenser must be thoroughly washed into the test solution after each determination, and then cleaned with alcohol.

The distillation flask is surrounded by a calcium chloride brine-bath maintained at 110° to 115° C. during the distillation; at a higher temperature excessive amounts of fatty impurities are carried over. The distillation proceeds smoothly and is complete when about 70 ml. of distillate have been collected in about 40 minutes. Failure to follow these directions exactly results in incomplete recovery unless the distillation is unduly prolonged, and also in great difficulty through frothing and bumping.

(ii) *The Optimum Amount of Oxidising Agent.*—Known amounts of diacetyl were steam-distilled from 500 ml. of the "underlying" solution containing various amounts of 40 per cent. (w/v) ferric chloride solution. The following results were obtained:

	Ferric chloride solution added ml.	Ferric chloride in underlying solution. Per Cent.	Diacetyl added equivalent to nickel dimethylglyoxime mg.	Nickel dimethylglyoxime found mg.	Number of determinations
(*a*)	250	20	17·1	15·0–14·6	2
(*b*)	250	20	8·55	6·6	1
(*c*)	100	8	8·55	8·4	1
(*d*)	25	2	8·55	8·8	1
(*e*)	None	None	17·1	17·0	2
	Distilled from underlying solution + butter freed from diacetyl				
(*f*)	250	20	17·1	17·1	1
(*g*)	250	20	8·55	7·8	1

The higher concentrations of ferric chloride (*a, b* and *g*) have a destructive effect on the diacetyl, which is less marked when the layer of butter is present.

A sample of butter (previously held at −10° C. for 6 months and containing an average amount of diacetyl + carbinol) gave the following results:

800 g. of butter over 500 ml. underlying solution containing

Ferric chloride (40% w/v) ml.	Ferric chloride in underlying solution Per Cent.	Nickel dimethylglyoxime found mg.
nil (distillation in CO_2)	nil	nil
10	0·8	1·1
25	2·0	1·1
50	4·0	1·5
250	20·0	1·4

While it has just been shown that excessive amounts of ferric chloride tend to decompose the diacetyl (under these conditions of distillation), on the other hand sufficient must be present to ensure maximum conversion of the carbinol into diacetyl; hence the concentration adopted throughout has been 50 ml. of 40 per cent. solution per 500 ml. underlying mixture (*i.e.* 4 per cent. ferric chloride solution). It is possible that butan-2:3-diol—the precursor of acetylmethylcarbinol—is, if present, also converted into diacetyl in this process.

III. THE SEPARATION OF DIACETYL FROM BUTTER BY DISTILLATION.—(i) *Apparatus and Method.*—As described in previous publications (Schmalfuss and Barthmeyer[5]; Michaelian, Farmer and Hammer[6]), this distillation is made in an atmosphere of carbon dioxide.

The apparatus is as previously described, except that an extra glass tube (i) projects about ½ inch through the treated rubber bung, and is tapered to a fairly fine jet. This is connected with a carbon dioxide generator, and the flask (containing the sample, sodium chloride, and $N/5$ sulphuric acid equal to one-fourth the volume of the butter taken) is flushed out with a strong stream of the gas for some minutes before the brine-bath, heated to about 115° C., is brought into place. As the butter melts, carbon dioxide is also introduced gently through the steam-inlet tube (ii), while the flow through (i) is gradually cut down. When frothing begins, the carbon dioxide is immediately cut off, and replaced by a strong current of steam, the effect of which is to cause the frothing to subside, although occasionally it may also be necessary to lower the brine-bath temporarily. The gas stream at (i) is cut down to a bubble or less per second, so as to maintain a slight outward pressure at the still-head and prevent diffusion of air into the flask.

(ii) *Results and Accuracy of the Determination.*—Two lots of butter, each 400 g., were steam-distilled over dilute acid for 2½ hours, and the final distillates were collected and found to be free from diacetyl. After cooling, 100 ml. of $N/5$ sulphuric acid and known amounts of diacetyl were added to each, 40 g. of sodium chloride were introduced, and the diacetyl was distilled, the flasks and contents being well cooled after each test. The following results were obtained:

Diacetyl added, mg.:	0·050	0·060	0·10	0·15	0·40	0·50	0·70	1·00	2·00	4·00	5·00
Equivalent to nickel dimethylglyoxime, mg.:	—	—	—	—	—	0·85	1·2	1·7	3·4	6·7	8·4
Nickel dimethylglyoxime found, mg.:	—	—	—	—	—	0·8	1·0	1·5	3·1	6·4	8·0
Equivalent to diacetyl, mg.:	0·035*	0·060*	0·12*	0·14*	0·38*	0·5	0·6	0·9	1·85	3·85	4·8

* Estimated colorimetrically.

The results are slightly low. Even the very gentle passage of carbon dioxide during the distillation appears to carry off a portion of uncondensed diacetyl. This explanation is probably correct, because very low results are obtained when a strong current of carbon dioxide is used throughout the distillation (Schmalfuss and Barthmeyer)[5]. The losses from butter are probably less than from artificial mixtures; nevertheless, as this determination of actual diacetyl is the more important of the two methods, it is under further investigation.

IV. PURIFICATION AND WEIGHING OF THE PRECIPITATE.—Notwithstanding the precautions recommended in the foregoing sections, these tedious operations may be to no purpose, unless the following technique is applied when washing the precipitate.

(i) *Transference and Washing of Precipitates.*—In an actual determination the distillate and condenser rinsings contain considerable amounts of fatty impurities (*e.g.* 0·3 to 2·4 mg. in one series), and at the beginning of the work these unnoticed impurities caused unduly high and puzzling results. This difficulty may be overcome in the following way:—For the gravimetric determination small Gooch crucibles are satisfactory; the asbestos mat, prepared from fibre digested in concentrated hydrochloric acid, is thoroughly washed with water (at least 10 fillings), and the precipitate of the red nickel compound is transferred, with thorough washing, from the beaker. The beaker (which usually still contains adhering precipitate) and the crucible are dried for 2 hours at 110° C. After cooling, the beaker is washed out on to the crucible with 30 to 40 ml. of ether, which has been recently distilled over flake caustic soda and charcoal. The dehydrated nickel compound is quite insoluble in this neutral, peroxide-free ether, and the fatty impurities are removed. The beaker and crucible are replaced for a short time in the oven until free from ether, and, when cool, are again thoroughly washed with water to remove any traces of precipitate and reagent, a "policeman" being used if necessary. The crucible is finally dried for 2 to 3 hours at 110° C. and allowed to cool in a desiccator. The use of alcohol or hot water for washing the precipitate, as recommended by some workers, must be avoided, as the nickel compound is appreciably soluble in both.

(ii) *Weighing.*—The cooled crucible is allowed to stand for 1 hour in the balance-case before weighing. (No drying agent is present in the balance-case.) Concordant weighings, occasionally varying by 0·1 mg. are thus obtained. The precipitate is dissolved by leaving the crucible half-filled with concentrated hydrochloric acid; the crucible is then thoroughly washed, dried at 110° C., and "conditioned" prior to being used again. It is practically impossible to avoid the inclusion of from 0·1 to 0·3 mg. of dust in the precipitate, leading to high results, unless an allowance is made by taking the tare weight of the crucible after that of the precipitate.

Calculations.

(i) Nickel dimethylglyoxime × 0·596 (*i.e.* 0·6 for small amounts) = *diacetyl.*

(ii) Nickel dimethylglyoxime × 0·610 = *acetylmethylcarbinol.* It is convenient to calculate this to diacetyl, instead.

(iii) The process of distillation with ferric chloride gives a precipitate equivalent to both acetylmethylcarbinol and diacetyl.

(iv) The process of distillation in carbon dioxide gives a precipitate equivalent to the actual flavouring substance, diacetyl.

(iii)—(iv) gives the flavourless precursor (carbinol) content.

V. A COLORIMETRIC METHOD FOR THE DETERMINATION OF TRACES OF NICKEL DIMETHYLGLYOXIME.—The amounts of diacetyl found in New Zealand butters have been minute, and mild-flavoured butters usually have a very low content of "total diacetyl" (carbinol + diacetyl).

The gravimetric determination of a few tenths of a milligram of precipitate is liable to involve a high percentage error, when the weighing is done on the usually four-place balance, and a colorimetric method suitable for amounts below 1 mg. of nickel dimethylglyoxime has therefore been devised.

The method outlined by Davies[3], in which the intensity of red colour given by the precipitate on the asbestos mat of a Gooch crucible is compared with the colours given by a standard series of precipitates, has not proved successful, owing to the facts that the precipitate comes down in both flocculent and crystalline form, the latter being of little colouring power, and that traces of precipitate are apt to be obscured under the particles of asbestos.

In the present method the nickel compound is dissolved in chloroform, and the resulting yellow solution is compared with standard solutions.

The colorimetric estimation of nickel dimethylglyoxime by dissolving it in chloroform and allowing the solvent to evaporate spontaneously, leaving a red stain which is compared with standards, was worked out by Bertrand and Macheboeuf.[8] It is not satisfactory for this work, because the amounts of precipitate are usually too large, and the evaporating solvent leaves a series of dark rings of precipitate interspersed with lighter areas.

(i) *Apparatus.*—As previously described.

(ii) *Method.*—When the precipitate is judged to be less than 1 mg. it is filtered by means of a King filter-stick,[9] and washed several times, and both beaker and filter-stick are dried for 2 hours in the oven at 100° C. When cold, the beaker is washed with 30 ml. of freshly-distilled ether, which is removed through the filter-stick, and the apparatus is again heated until the ether has evaporated. After cooling, the washing with water is repeated, the inner glass tube and rubber connector are removed from the filter-stick, and the outer tube (which carries the asbestos and precipitate) and beaker are dried at 110° C. When nearly cold, 10 ml. of recently distilled neutral chloroform are added, and the beaker is covered with a watch-glass and warmed gently. When solution is complete, it may be necessary to filter the cooled solution (from asbestos fibres) through a plug of cotton wool into the small Nessler tube (specimen tubes with plane ends, selected so that the 10-ml. marks are of even height, are suitable for the purpose). The colours are compared in the usual way with standard solutions of nickel dimethylglyoxime in chloroform. The standard solution does not keep, particularly in the light, owing to the formation of acidic substances from the chloroform.

The solubility of the nickel compound is only 14·8 mg. per 100 ml. at 14° C., and concentrations higher than 1·0 mg. per 10 ml. are rather too dark for comparison. The faint yellow colour of the smaller amounts is not suitable for measurement in a tintometer or colorimeter.

It has since been found that tetrachloroethane is the only common solvent in which the nickel compound is more soluble than in chloroform (solubility in tetrachloroethane 28 mg. per 100 ml. at 16·5° C.).

Experiments with the Colorimetric Method.—With large volumes of solution and fresh reagents the results are slightly low. For example, in experiments in which 0·20 mg. of diacetyl were added, the following results were obtained:

	After 24 hrs. mg.	48 hrs. mg.	72 hrs. mg.	144 hrs. mg.
(*a*) 10 ml. of fresh reagents in 50 ml. total volume	0·15	0·16	0·14	0·17
(*b*) 10 ml. of fresh reagents in 10 ml. total volume	0·16	0·17	0·18	0·18

Another experiment, in which the precipitates were allowed to stand for 10 days before filtering, gave the following results:

Diacetyl added, in 10 ml. (mg.)	nil	0·05	0·10	0·20	0·40	0·60
,, found, in 10 ml. ,,	nil	0·025	0·068	0·15	0·32	rather dark for comparison, but about equal to standard.
,, loss, in 10 ml. ,,	—	0·025	0·032	0·05	0·08	

The losses are parallel with the amounts of precipitate and, strictly, are not solubility losses.

In order to compensate for the solubility, the mixed reagents were saturated with nickel dimethylglyoxime by boiling and allowing the precipitate to form in the usual way for 10 days before filtering. Determinations by means of this reagent in a series of tests similar to those described (0·05 mg. of diacetyl and upwards) gave results in which the standards were satisfactorily matched, although tending to be high.

Preparation of Reagent.—The following method of preparing the saturated reagent has now been adopted:*

The filtrates from a number of diacetyl determinations are concentrated to the original volume of reagent-solution (*i.e.* 10 ml. per determination), ammonia is added, and the solution is allowed to stand for as long as possible before filtering from a minute quantity of impurity (in which only a trace of nickel dimethylglyoxime is usually detectable). Hydroxylamine hydrochloride is added to bring the solution back to its original strength, the hydroxylamine-content being conveniently found by the method given in the *B.D.H. Book of A.R. Standards*.

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* The use of recovered reagent and evaporation to the 10-ml. mark on a hot-plate [*cf.* Part I (i)] are now followed in all determinations, and the risk of missing minute amounts is thereby avoided.

The results obtained by the use of this reagent are invariably a shade high, and control tests made on one lot of reagent gave:

Diacetyl added (mg.)	0·050	0·10	0·20	0·40	Blank, 10 ml. of reagent only.
„ found „	0·055	0·111	0·22	0·425	—
Correction to be deducted (mg.)	0·005	0·01	0·02	0·03	<0·002

Control determinations should be carried out with each lot of reagent, as the corrections are of a different order for various recovered reagents. The ordinary "blank" determination is of no value. The actual results obtained (which are corrected) are given in Parts I and III (pp. 654, 658).

The presence of the dissolved nickel dimethylglyoxime seems to hasten the precipitation. In one experiment 0·20 mg. of diacetyl gave the following amounts of precipitate with the saturated reagent:

	24 hours	48 hours	72 hours	48 hours
Diacetyl found, mg.	0·20	0·18	0·20	0·20 (corrected)

Nevertheless, it is preferable to allow the solution to stand for several days before filtering.

By using this technique and smaller amounts of butter, this method could be adapted for control purposes of the "total diacetyl," and results of fair accuracy would be obtained within about 48 hours after distillation.

GENERAL REMARKS.—*The Effect of Diacetyl on the Oxidation of Butter-fat.*—Great emphasis is laid by some writers on the pro-oxidative effect of diacetyl on butter-fat and the vitamins. The work of King[10] is the only investigation, so far as I am aware, which deals with this point, and his lowest concentrations of diacetyl examined were 50 p.p.m., which scarcely affected his samples of butter-fat after 90 to 100 days in the dark at 22° C. As the diacetyl-content of butters of the highly-flavoured type never exceeds 4 p.p.m. (*loc. cit.*), it is not considered that diacetyl itself is responsible for the poorer keeping qualities of "ripened" cream butter.

The Effect of the Age of the Sample upon its Diacetyl-content.—Results obtained with butter made from slightly "ripened" cream were as follows:

	Carbinol + diacetyl p.p.m.
Butter A (3 months frozen storage)	1·0
Butter A (4 months further keeping at room temperature; quite tallowy)	0·6
Butter B (2 months frozen storage)—4 p.p.m. diacetyl added for experimental purposes	4·8
Butter B (6 months further keeping at room temperatures; very tallowy, bleached throughout and "cheesy"; inedible)	1·1

The loss is not as great as might be expected.

THE DETECTION OF ADDED DIACETYL IN BUTTER.—It has been stated (Davies[3]) that "the finding of a relatively high diacetyl-content in association with a low acidity of butter should be viewed with suspicion. . . ." As most butter factories in New Zealand, Australia and U.S.A. neutralise their cream before churning, it is difficult to see that either the acidity or *p*H value of the butter could be regarded as a reliable indication of the acidity developed before neutralisation, although there is an approximate relationship with the acidity at churning (F. H. McDowall, unpublished work). It is more likely that the ratio of the diacetyl to carbinol + diacetyl (which in New Zealand butters is low) would be of more value, unless both diacetyl and carbinol were added, in which case the problem of detecting such sophistication would appear to be insoluble, unless bacteriological determinations gave any guide as to whether a "starter" had been used in the cream from which the butter was churned.

In any case, it would seem that the problem of detecting added diacetyl in butter is likely to be difficult, particularly until more is known about the range of concentration to be expected in genuine butter obtained from numerous countries and manufactured under various conditions.

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The Determination of Moisture in Cereal Products by Distillation with Tetrachloroethane

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(*Read at the Meeting of the North of England Section, February* 9, 1935)

INTRODUCTION.—The different types of moisture present in cereal products cause widely different results to be obtained by different methods of estimation. Snyder and Sullivan,[1,2] in a series of investigations into the moisture-content of flour by different methods, suggested three stages of drying, during which the following types of moisture are removed:—(1) Free; (2) adsorbed; (3) loosely chemically combined. Fisher[3] suggested similar stages, as the result of a study of the rate of drying of flour over sulphuric acid.

It appears that the drying of flour at 100° C. at normal pressures drives off the first, and part of the second, type. The third type is removed only at 120° C. to 130° C. at ordinary pressures, or at 100° C. under greatly reduced pressure. Interaction with calcium carbide leaves about 4·5 per cent. of non-reacting moisture, as compared with the vacuum-oven method at 100° C.[4]

Of the distillation methods, that of Duval[2] consists in distilling the water from high-boiling paraffin, and is a troublesome process. Immiscible solvents which distil with the water have been suggested, *e.g.* toluene, xylene, light petroleum (b.p. 104° C.), tetrachloroethane and mixtures of these. The lower-boiling liquids take hours to carry over all the water,[5] whilst the higher-boiling liquids may cause liberation of water by decomposition. Tausz and Rumm[6] and Fairbrother and Wood[7] describe methods of distillation with tetrachloroethane for products containing fairly large amounts of moisture, and give figures in comparison with those obtained by oven methods. In neither paper, however, is the question of possible carbohydrate decomposition considered.

Our purpose was to find a method suitable for baked cereal products (of low moisture-content) and for unbaked materials, the results for which could be correlated with baking losses.

EXPERIMENTS

(1) PROPORTION OF T.C.E. REQUIRED.—Our first trials consisted of interrupted distillations of liquid and sample in different proportions. The distillations were carried on for a fixed time and then stopped. The volume of water was read off, and the distillation was continued for a further period, until no more tetrachloroethane could be distilled. Typical results are shown in Table I.

It is evident that, with sufficient liquid present, all the moisture can be distilled in 6 minutes, and that no decomposition takes place after a further 4 minutes' boiling. An amount of liquid insufficient to keep the contents of the flask mobile results in progressive decomposition and in a progressive increase in the amount of water distilled. At least 3 times as much tetrachloroethane as sample is required when distilling from a large quantity of sample.

TABLE I

THE EFFECT OF DIFFERENT PROPORTIONS OF LIQUID AND SAMPLE

Weight of sample g.	Tetrachloroethane ml.	Time of distillation Minutes	Volume of water distilled ml.	Volume of tetrachloroethane distilled ml.
180	350	6	Nil	
		9	1·95	
		12	2·55	
		15	2·85	270
150	350	3	2·1	
		6	2·7	
		9	2·7	
		10	2·8	245
150	450	3	1·9	
		6	2·4	
		9	2·4	
		12	2·4	300
50	250	5	6·75	
		6	6·9	
		7	6·9	
		10	6·95	200

(2) THE RATE OF DISTILLATION.—As decomposition can readily be caused to take place, it seemed advisable to determine how slowly the moisture could be distilled without influencing the result. Some results are shown in Table II. These were also interrupted distillations.

TABLE II

THE EFFECT OF THE RATE OF DISTILLATION

Weight of sample g.	Tetrachloroethane ml.	Time of distillation Minutes	Water distilled ml.	Rate of distillation ml. per minute
150	400	3	2·5	15
		6	3·0	
		9	3·1	
		12	3·2	
		15	3·3	
100	300	7	3·00	15
		8	3·15	
		9	3·20	
150	450	3	1·9	25
		6	2·4	
		9	2·4	
		12	2·4	
150	450	4	1·95	25
		6	2·0	
		8	2·0	
		10	2·0	

All the water is not driven off within 10 minutes when the rate of distillation is slow, and decomposition of carbohydrate material appears to take place after

10 minutes at the temperature of the boiling mass. This is contrary to the results of Tausz and Rumm, who distil slowly through a special still-head. Our results were obtained on biscuit material. The large quantities of sample were necessary because of the low moisture-contents.

(3) FINAL CHECK.—Having fixed the two conditions necessary to give consistent results, straight distillations of different portions of sample, taken from the same bulk, were made for times varying from 6 to 10 minutes. The following results were obtained:

TABLE III

Weight of sample. g.	Tetrachloroethane ml.	Time of distillation Minutes	Water distilled ml.
150	450	8	3·4
		8	3·3
		10	3·4
100	300	5	4·95
		6	4·95
		8	4·95
100	300	8	4·00
		8	4·05
		8	4·05

These duplicates agree as well as those obtained by any oven method, and, as will be seen later, bear a definite relationship to the boiling water oven figures.

METHOD OF DETERMINATION.—*Quantity of Sample.*—Sufficient sample to yield 2–5 ml. of water should be taken (usually 30–100 gms.). These quantities may be decreased somewhat if the sensitivity of the measuring apparatus is increased.

Preparation of the Sample.—As it is necessary to distil over the water in less than 10 minutes when carbohydrate material is present, the sample should be in a sufficiently fine condition to permit of the liberation of the water in this time. Meal and flour distil satisfactorily, whilst biscuit, cake, etc., should be ground and quickly transferred to the boiling-flask.

Quantity of Tetrachloroethane.—This will depend on the amount of the sample and on the technique used. There must be sufficient liquid left in the flask, after the water has been distilled, to keep the mass fluid and so prevent charring. Too much liquid slows up the distillation of the water. Generally, about 150 ml. for 30 g. of sample to 300 ml. for 100 g. are advisable.

Distillation Technique.—The sample and liquid are thoroughly mixed in a suitable boiling-flask connected by an ordinary cork or ground-glass connection to a still-head having a wide bore at its lower end to prevent splashing at the rate of distillation required. This is connected with a vertical condenser having a burette, partly filled with tetrachloroethane, fixed at the outlet. The tetrachloroethane is distilled at the rate of 20 to 25 ml. per minute. The water collects at the top of the distillate, and the level of liquid in the burette is maintained by a suitable adjustment of the burette-tap. When almost all the moisture has been distilled, the distillate, which is milky at first, suddenly clears. The distillation is continued for about a minute longer, when the cooling water of the condenser is turned off. Heating is continued until the tip of the condenser becomes hot, when the gas is removed. The volume of water in the burette is measured, after cooling, by taking the readings of the top of the top meniscus and the bottom of the water and tetrachloroethane junction.

Another satisfactory technique is the use of the still-head of the American Association of Petroleum Technologists, described also by Fairbrother and Wood.[7] Tetrachloroethane is first introduced into the graduated portion and, on distilling, the water collects on this column, whilst the tetrachloroethane returns to the flask. Less tetrachloroethane is required by this method, as there is no loss from the flask.

Both types of still-head need an internal diameter of at least ⅜ inch, and no constriction between the bulbs should be less than this.

Comparative results obtained by the method and by the use of the water-oven are shown in Table IV.

TABLE IV

COMPARISON BETWEEN THE DISTILLATION AND WATER-OVEN RESULTS

		Moisture		
		Distillation Per Cent.	Oven at 98·5° C. Per Cent.	Difference
Flour.				
	Manitoba	13·8	12·05	1·75
	Blend	13·15	11·2	1·95
	Australian	13·2	11·4	1·8
	English	14·25	12·45	1·8
				1·8
Baked products.				
	Bread (crumb) ..	49·6	48·0	1·6
		49·3	47·9	1·4
		48·3	47·0	1·3
				1·4
	Cake	5·7	4·5	1·2
		1·9	1·0	0·9
		4·0	2·7	1·3
				1·1
	Biscuit	2·25	1·0	1·25
		4·95	4·2	0·7
		2·50	1·70	0·8
		2·10	0·75	1·4
		Average of 30–40 tests		0·7
Fat—Cane sugar—Water systems.				
		25·1	25·1	Nil
		19·6	19·6	Nil
Cane syrups.	Steady decomposition.			

COMMENTS ON THE RESULTS.—The results for cereals appear to be similar to the maxima obtained by oven methods, and, at the same time, avoid the oxidation errors of the oven methods. The difference between the distillation and water-oven methods becomes less as dehydration by baking proceeds. The value of the method lies in the fact that a determination can be completed within about 15 minutes of the receipt of the sample.

SUMMARY AND CONCLUSIONS.—Accurate and reproducible results for moisture in cereal products of low moisture-content can be obtained by distillation with tetrachloroethane (b.p. 140° C.).

The essential conditions are moderately rapid distillation and sufficient solvent to leave a mobile residue when all the water has been driven off.

The results obtained for flour are 1·8 per cent. higher than those obtained by heating in a water-oven for 5 hours.

The method is not satisfactory when appreciable quantities of invert sugar are present.

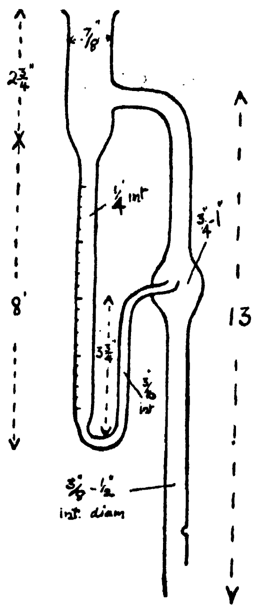

Fig. 1

Our thanks are due to Messrs. William Crawford & Sons, Ltd., for permission to publish these results.

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NOTE.—Since the paper was read a modified form of the continuous still-head has been used. This is shown in Fig. 1 above. The volume measurement is more accurate in this, and the return has been arranged so that a bubble of water cannot readily remain on the cold tetrachloroethane, as sometimes happened with the original apparatus. All diameters are internal measurements.

FAIRFIELD BISCUIT WORKS
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The Oxalates of Calcium, Strontium, Barium, and Magnesium

By J. HASLAM, M.Sc., A.I.C.

(Read at the Meeting of the North of England Section, October 12, 1935)

Goy[1] found that when calcium oxalate is precipitated in the usual way from boiling solution the precipitate has the composition $Ca(COO)_2.H_2O$, and that this precipitate can be completely freed from adherent moisture, without loss of water of crystallisation, by filtration on a Gooch crucible, and drying for four hours at 100–105° C. From a cold solution, however, a mixture of $Ca(COO)_2.H_2O$ and $Ca(COO)_2.3H_2O$ is obtained.

Dick[2] has endeavoured to use this method as a rapid and accurate means of determining calcium as calcium oxalate monohydrate by filtering off the precipitate on a sintered glass crucible, removing adherent moisture by washing with alcohol and with ether, and weighing the precipitate after removal of the ether by suction or *in vacuo*.

Moser[3] tested Dick's method, but obtained results from 1·6 to 3 per cent. too high; he found it to be impossible to remove the whole of the adherent moisture except by actual drying in ovens.

Our own experiments were concerned with the relationship between the weight of the calcium oxalate precipitate and the titration of this precipitate in terms of standard potassium permanganate solution, and, further, the effect of the presence of barium, strontium or magnesium on this relationship.

To a known volume of standard calcium solution (pure Iceland spar dissolved in dilute hydrochloric acid) were added 5 ml. of concentrated hydrochloric acid and about 100 ml. of distilled water, followed by 20 ml. of saturated ammonium oxalate solution.

When a precipitate was produced in the cold, concentrated hydrochloric acid was added in 5-ml. portions until a perfectly clear liquid was obtained. This liquid was now diluted to 200 ml. and heated to boiling, and concentrated ammonia solution was added to the boiling liquid until it was just ammoniacal to methyl orange. The precipitate was digested by immersing the covered beaker in a boiling water-bath for ¾ hour, allowed to stand overnight, and then filtered off on a sintered glass crucible (1.G.3), washed five times with 0·1 per cent. ammonium oxalate solution (at about 50° C.), drained by suction, washed five times with water (at about 50° C.), and again drained by suction.

Adherent moisture was removed by washing five times with absolute alcohol (5 ml. each time), then draining, using the full suction of the vacuum pump, for two minutes. The washing was completed by treating the precipitate four times with ether (5 ml. each time), then draining, using the full suction of the vacuum pump, for five minutes. The crucible was wiped, placed in the desiccator for a few minutes, and then weighed.

Our results having confirmed Moser's conclusions as to the high results obtained by Dick's method, we titrated the oxalate ion in the precipitates as follows:

The sintered glass crucible containing the precipitate was placed in a large beaker (capacity 600 ml.), about 100 ml. of water were added, and then 20 ml. of dilute (20 per cent. by volume) sulphuric acid solution, the whole was diluted to 200 ml., and heated on the water-bath to about 70° C., and the permanganate titration was carried out as usual.

In the titrations with *N*/10 permanganate solution the odour of aldehyde could always be detected; this indicated the presence of traces of alcohol in the precipitates as weighed, which would, of course, tend to produce high results (both by weight and titration).

We therefore decided to heat the calcium oxalate precipitates at 100° C. to remove this alcohol, before proceeding to the permanganate titration. We found that the precipitates attained constant weight in the course of about one hour, and it has since been stated by Brunck[4] that the precipitate thus obtained (in his case dried at 105 to 110° C.) corresponds with $CaC_2O_4.H_2O$ in composition, and that this method of determination of calcium is comparable in accuracy with the ordinary methods; he does not, however, give any experimental results in support of this contention.

In our experiments, however, we noticed that after the precipitates had been heated to constant weight at 100° C., there was a slight discrepancy between the theoretical permanganate titration (assuming the dried precipitate to consist of pure $CaC_2O_4.H_2O$), and that actually obtained. The following results are typical:

Calcium oxide added g.	Calcium oxalate precipitate obtained by Dick's method g.	Calcium oxalate precipitate, after drying to constant weight at 100° C. (one hour) g.	Titration of dried calcium oxalate ppt., *N*/10 $KMnO_4$ ml.	Theoretical titration, assuming dried precipitate to consist of pure $CaC_2O_4.H_2O$, *N*/10 $KMnO_4$ ml.	Theoretical titration corresponding to calcium oxide added, *N*/10 $KMnO_4$ ml.
0·05882	0·1539	0·1536	21·0	21·03	20·97
0·1174	0·3075	0·3071	41·90	42·05	41·87
0·2932	0·7682	0·7676	104·55	105·1	104·6
0·2932	0·7683	0·7675	104·55	105·1	104·6

During the past two years we have carried out numerous comparisons along these lines, but we have always noticed the same general tendency, *i.e.* that the results obtained by the gravimetric method, even after the calcium oxalate precipitate has been dried to constant weight, are too high, and where large amounts of calcium oxide are in question (of the order of 0·3 g.) the use of this method may give rise to serious errors.

Briefly, we believe that the titration of the oxalate ion gives the most reliable indication of the amount of calcium in the precipitate, particularly where sintered glass crucibles are used, instead of filter paper, in the filtration of the precipitate.

STRONTIUM.—Strontium carbonate was carefully purified from barium and calcium and dissolved in dilute hydrochloric acid, and this solution was used in our experiments.

The following points should be noted in connection with the precipitation of strontium as oxalate:

(1) The precipitated strontium oxalate consists essentially of $SrC_2O_4.H_2O$. A precipitate weighing 0·5384 g., obtained after washing with alcohol and ether as in the calcium experiments, gave, after being heated for one hour at 100° C. to remove alcohol, a permanganate titration of 54·7 ml. of $N/10$ potassium permanganate solution. (Theoretical for pure $SrC_2O_4.H_2O$ = 55·6 ml. of $N/10$ permanganate solution.)

(2) The precipitated oxalate is not stable in an electric oven maintained at 100 ± 2° C.; 0·5387 g. of the precipitate lost 0·0479 g. after twenty-four hours at this temperature.

(3) Owing to the interference of insoluble strontium sulphate produced in the course of the titration, the oxalate, after being dried, does not show its full titration value in the sulphuric permanganate titration.

Thus, 0·5384 g. of the precipitate obtained after washing with alcohol and ether gave 0·5118 g. $SrSO_4$, corresponding with 55·72 ml. of $N/10$ permanganate solution. Actually, after drying to remove alcohol, the titration gave 54·7 ml. of $N/10$ permanganate from a corresponding amount of the strontium oxalate precipitate.

(4) Strontium is not completely precipitated as oxalate under conditions similar to those for complete precipitation of calcium.

Strontium oxide added g.	Strontium oxalate precipitated by Dick's method g.	Titration of dried strontium oxalate precipitate, $N/10$ $KMnO_4$ ml.	Theoretical titration corresponding with strontium oxide added, $N/10$ $KMnO_4$ ml.
0·0592	0·0980	10·02	11·42
0·1183	0·2090	21·57	22·83
0·2958	0·5384	54·7	57·10

BARIUM.—The barium solution used was prepared from $BaCl_2.2H_2O$ (Analar). The oxalate, precipitated under conditions similar to those outlined for calcium on p. 668, possesses essentially the composition $BaC_2O_4.\frac{1}{2}H_2O$.

The precipitated oxalate does not behave normally in the ordinary sulphuric acid permanganate titration, because the insoluble barium sulphate produced probably forms an external coating on the large crystals of barium oxalate, and this prevents the full realisation of the permanganate titration. However, if perchloric acid is substituted for sulphuric acid, the oxalate ion may be titrated without interference.

Thus, 0·3914 g. of the precipitate obtained, after washing with alcohol and ether as in the calcium experiments, gave a permanganate titration of 33·3 ml. of $N/10$, alcohol being removed by drying at 100° C. prior to the titration. This titration is equivalent to 38·28 per cent. of $(COOH)_2$.

Calculated for $Ba(OOC)_2.\frac{1}{2}H_2O$ = 38·40 per cent. of $(COOH)_2$.

Further, 0·4271 g. of the above precipitate yielded 0·4253 g. of barium sulphate = 65·37 per cent. of barium oxide.

Theoretical for $Ba(OOC)_2.\frac{1}{2}H_2O$ = 65·4 per cent. of barium oxide.

The precipitate appears to be fairly stable at 100° C., in which respect it resembles the corresponding calcium precipitate more closely than the strontium precipitate.

Under the normal conditions of complete precipitation of calcium, barium is very incompletely precipitated, as the following results show:

Barium oxide added g.	Barium oxalate obtained by Dick's method g.	Barium oxalate obtained after drying for one hour at 100° C. g.	Theoretical titration, assuming dried precipitate to consist of $BaC_2O_4.\frac{1}{2}H_2O$, $N/10$ $KMnO_4$ ml.	Titration of dried barium oxalate ppt., $N/10$ $KMnO_4$ ml.	Theoretical titration corresponding with barium oxide added, $N/10$ $KMnO_4$ ml.
0·0601	0·0722	0·0719	6·13	1·0	7·84
0·1201	0·1587	0·1584	13·52	4·65	15·66
0·3003	0·4260	0·4256	36·32	13·3	39·15

MAGNESIUM.—In these experiments, magnesium ammonium chloride (Analar) was used as the source of magnesium.

It was found that magnesium was precipitated essentially as $MgC_2O_4.2H_2O$. Thus, 0·5371 g. of the precipitate obtained after drying for one hour at 100° C. gave a permanganate titration of 71·85 ml. of $N/10$ $KMnO_4$, corresponding to 60·20 per cent. of $(COOH)_2$. Calculated for $MgC_2O_4.2H_2O$ = 60·67 per cent. of $(COOH)_2$.

Again, 0·2594 g. of the above dried precipitate yielded 0·5407 g. of magnesium hydroxyquinoline complex, $Mg(C_9H_6ON)_2$, corresponding with 16·22 per cent. of magnesium. Calculated for $MgC_2O_4.2H_2O$ = 16·40 per cent. of magnesium.

Of course, in the presence of ammonium chloride, magnesium oxalate is comparatively soluble, but even so, as is well known, it is also very liable to be carried down with calcium in an oxalate precipitation, and a double precipitation of calcium should always be carried out in the presence of magnesium.

PRECIPITATION OF CALCIUM IN THE PRESENCE OF BARIUM, STRONTIUM AND MAGNESIUM.—Known amounts of calcium were precipitated in the presence of known amounts of barium, strontium and magnesium, as outlined in the method on p. 668.

The following results were obtained:

Composition of mixture	Oxalate precipitate		Titration of dried oxalate ppt., $N/10$ $KMnO_4$ ml.	Calculated titration, assuming dried precipitate to consist of pure $CaC_2O_4.H_2O$, $N/10$ $KMnO_4$ ml.
	obtained by Dick's method g.	after drying for 1 hour at 100° C. g.		
0·2932 g. CaO 0·0594 g. SrO	0·8754	0·8744	114·95	119·8
0·2932 g. CaO 0·0601 g. BaO	0·8298	0·8275	108·83	113·3
0·2932 g. CaO 0·5 g. MgO	0·8083	0·8059	109·25	110·4

We have already pointed out that a slight discrepancy exists between the weight of a dried calcium oxalate monohydrate precipitate and its permanganate titration value, but the above results certainly indicate that this relationship is seriously affected by the presence of barium or strontium in the oxalate precipitate, and to a less degree by the presence of magnesium.

One interesting fact that has been observed is that the contamination of a precipitate of calcium oxalate with even very small proportions of magnesium always tends to cause the precipitate to adhere to the sides of the glass vessel used in the precipitation; with pure calcium oxalate this effect has not been observed.

I have to thank Mr. F. Sweeney for help in connection with the experimental work, and the directors of Imperial Chemical Industries, Ltd., for permission to publish the results of this investigation, which was carried out in the Research Department of their subsidiary company, I.C.I. (Alkali), Ltd., Northwich.

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Electrometric Determination of Thallium

BY WINIFRED R. A. HOLLENS, PH.D., AND JAMES F. SPENCER, D.SC.

SEVERAL methods for the electrometric determination of thallium are recorded in the literature; the most important are those due to Zintl and Rienäcker[1] and C. del Fresno and Valdés.[2] The reaction used by the former workers consists in the oxidation of the thallous ion by titration with potassium bromate using a platinum electrode and a N. calomel electrode to indicate the end-point. A second method due to the same authors involves the reduction of the thallic ion by means of titanous chloride in the presence of ammonium acetate, the same electrode system being employed. Fresno and Valdés oxidise the thallous ion by titration with potassium ferricyanide in alkaline solution.

The results of the latter authors are frequently 1·0 per cent. low, whilst the methods of Zintl and Rienäcker are rather involved. The bimetallic electrode system has been shown (Spencer and Pring[3]) to furnish accurate values for the titration of iodine by sodium thiosulphate and sodium arsenite, in connection with the electrometric determination of copper. Consequently, since thallium in the higher state of oxidation behaves like copper in its reaction with potassium iodide, it was decided to investigate the reaction as a possible means for the electrometric determination of thallium.

The method, which proved to be satisfactory, consists in converting the thallium to the higher state of oxidation, adding a suitable quantity of potassium iodide, and titrating with either sodium thiosulphate or sodium arsenite of concentration approximately equivalent to that of the thallium, and determining the end-point by means of the Foulk and Bawden[4] bimetallic electrode system. In this case it was found that a potential of 15 millivolts imposed upon the electrodes gave a sharp and accurate end-point, provided that the electrodes were depolarised before use.

OXIDATION OF THALLIUM TO THE THALLIC STATE.—A solution of a thallous salt was precipitated as chloride and treated in the cold with washed chlorine until it had completely dissolved. A current of air was then bubbled through the solution to remove the dissolved free chlorine, until the emerging gas failed to react with starch iodide paper.

I. TITRATION WITH SODIUM THIOSULPHATE.—A series of titrations was carried out with solutions of thallic ion of concentration varying from 0·2 *N* to 0·002 *N*. A measured volume of the thallium solution was rendered slightly acid with acetic acid, an excess of potassium iodide solution was added, and the liberated iodine was titrated. It was also found that the liberated iodine could be satisfactorily titrated without electrodes by adding about 10 ml. of chloroform and titrating with sodium thiosulphate solution of normality approximately equivalent to that of the thallium, and shaking until the colour of iodine disappeared from the chloroform layer. The results of six series of titrations are recorded in Table I.

TABLE I

	25 ml. 0·2 *N* $TlCl_3$+ 2 g. KI + CH_3CO_2H		25 ml. 0·1 *N* $TlCl_3$+ 2 g. KI + CH_3CO_2H		25 ml. 0·05 *N* $TlCl_3$+ 2 g. KI + CH_3CO_2H	
Indicator.	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Thiosulphate used	25·10	25·20	25·15	25·20	25·10	25·25
,, ,,	25·15	25·25	25·15	25·30	25·10	25·20
,, ,,	25·15	25·20	25·20	25·20	25·15	25·23
Average ..	25·13	25·22	25·17	25·23	25·12	25·23

	25 ml. 0·01 *N* $TlCl_3$+ 1 g. KI + CH_3CO_2H		25 ml. 0·004 *N* $TlCl_3$ + 1 g. KI + CH_3CO_2H		25 ml. 0·002 *N* $TlCl_3$+ 1 g. KI + CH_3CO_2H	
Indicator	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Thiosulphate used	25·25	25·25	25·10	25·25	No satis-	25·25
,, ,,	25·30	25·25	25·10	25·25	factory	25·25
,, ,,	25·35	25·30	25·20	25·23	end-point	25·30
Average ..	25·30	25·27	25·15	25·23		25·27

The calculated volume of sodium thiosulphate solution required in all cases is 25·25 ml.

The normalities of thallic chloride given in the table are only approximate. A litre of the solution, named 0·2 *N*, was made from 23·8510 g. of thallous chloride, and the other solutions were prepared by diluting this as shown. The thiosulphate solution used with the 0·2 *N* thallium solution was 0·1968 *N*, and the solutions used in other cases were prepared by diluting the former to the same extent as the thallium solution.

The electrometric titrations show that, for concentrations down to 0·002 *N*, this method furnishes results which are accurate to 2 parts in 2,500, but at greater dilution the results are much less accurate. The results with chloroform as indicator are generally not so accurate, but even here values which differ by only about 0·25 per cent. from the calculated value are obtained. This is due to the fact that the end-point is difficult to determine, because the thallous iodide adsorbs iodine, giving a greenish precipitate and making the disappearance of the colour in the chloroform a little uncertain. The method breaks down entirely at a concentration of 0·002 *N* thallic chloride.

EFFECT OF CONCENTRATION OF ACETIC ACID.—The effect of varying the amount of acetic acid added is given in the table below (Table II).

TABLE II

25 ml. 0·1 *N* $TlCl_3$ + 2 g. KI. Electrometric indication

Acetic acid added	None ml.	A few drops of 0·1 *N* acid ml.	2 ml. 2 *N* acid ml.	5 ml. glacial acetic acid ml.
Thiosulphate used	28·75	28·75	28·75	28·75
,, ,,	28·75	28·75	28·73	28·75
,, ,,	28·80	28·70	28·70	28·71
Average ..	28·77	28·73	28·73	28·74

The calculated volume of sodium thiosulphate required is 28·72 ml. A litre of the thallium solution was prepared from 12·3010 g. of thallous chloride, and the thiosulphate solution in this case was 0·0893 *N*. The results indicate that the concentration of the acetic acid may be varied over a very wide range, but that the presence of the acid is not essential.

EFFECT OF ACIDS OTHER THAN ACETIC ACID.—A further series of titrations was carried out with sulphuric and hydrochloric acids, respectively, and the results given below were obtained. Twenty-five ml. of thallic chloride solution (prepared by oxidising 12·6816 g. of thallous chloride and making up to 1 l.) and 2 g. of potassium iodide were used in each titration. The calculated volume of sodium thiosulphate is 28·34 ml.

	5 ml. 2 *N* acetic acid		5 ml. 2 *N* HCl		5 ml. 2 *N* H_2SO_4	
Indicator	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Thiosulphate used	28·30	28·25	28·35	28·45	28·35	28·40
,, ,,	28·35	28·30	28·30	28·40	28·35	28·42
,, ,,	28·35	28·30	28·35	28·40	28·30	28·40
Average ..	28·33	28·28	28·33	28·42	28·33	28·41

The end-point is a little high with the solutions containing hydrochloric and sulphuric acids, owing doubtless to the higher hydrogen ion concentration of these solutions, but even here the divergence from the calculated value is rather less than 0·3 per cent. The results with chloroform as indicator are considerably better.

TITRATION IN THE PRESENCE OF OTHER METALS.—Experiments were performed to ascertain whether thallium can be determined by the above method in the presence of any or all of the metals which usually accompany it in its commercial form. The metals examined were zinc, lead, iron and copper. Known amounts of a soluble salt of these metals were added to a known solution of thallium, and the titration was performed as described above.

Twenty-five ml. of 0·1 *N* zinc chloride solution were added to 25 ml. of thallic chloride solution containing 2 g. of potassium iodide and 2 ml. of 2 *N* acetic acid.

	$TlCl_3$ ml.	$TlCl_3 + ZnCl_2$ ml.
Thiosulphate used	25·96	25·95
„ „	25·96	25·97
Average ..	25·96	25·96

The result in the presence of zinc is identical with that in its absence.

Solutions containing lead acetate in addition to thallic chloride gave no satisfactory end-point.

Ten ml. of 0·1 *N* ferrous ammonium sulphate solution were added to 25 ml. of thallic chloride solution containing 2 g. of potassium iodide. No acid was added in this case.

	$TlCl_3$		$TlCl_3 + FeSO_4(NH_4)_2SO_4.6H_2O$	
Indicator	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Thiosulphate used	25·15	25·20	25·25	24·20
„ „	25·15	25·30	25·20	25·25
„ „	25·20	25·20	25·20	25·25
Average ..	25·17	25·23	25·22	25·23

Attempts were made to determine thallium in the presence of ferric iron by Spencer and Pring's[3] method for copper, but were unsuccessful.

Twenty-five ml. of 0·1 *N* copper sulphate solution were added to 25 ml. of thallic chloride solution containing 2 g. of potassium iodide and a little acid.

	25 ml. $CuSO_4$ ml.	25 ml. $TlCl_3$ ml.	25 ml. $CuSO_4$ +25 ml. $TlCl_3$ ml.
Thiosulphate used ..	13·59	26·59	40·14
„ „	13·60	26·60	40·16
Average	13·59	26·59	40·15

The calculated quantity of sodium thiosulphate required is 40·18 ml.

These results show that the sum of the thallium and copper may be determined by this method, and, if the copper is determined electrolytically or by some other method, the value for thallium becomes known.

II. TITRATION WITH SODIUM ARSENITE.—A series of experiments was carried out to ascertain the suitability of the bimetallic electrode system to the titration of the iodine, liberated by thallic salts from potassium iodide, by sodium arsenite. It is essential that the solution should be alkaline during the titration. In the present case it has been found necessary to liberate the iodine before the addition of sodium bicarbonate, thereby preventing the precipitation of thallic hydroxide. The titration was carried out as described above, using both chloroform and electrometric indicators to ascertain the end-point. The results are recorded in the table below.

	25 ml. 0·1 *N* $TlCl_3$		25 ml. 0·02 *N* $TlCl_3$	
Indicator	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Sodium arsenite used	26·00	26·00	26·00	26·00
,, ,, ,,	26·00	25·95	26·02	25·98
.. .. ..	26·00	25·93	25·99	25·97
Average ..	26·00	25·96	26·00	25·98

	25 ml. 0·01 *N* $TlCl_3$		25 ml. 0·002 *N* $TlCl_3$	
Indicator	$CHCl_3$ ml.	Electrometric ml.	$CHCl_3$ ml.	Electrometric ml.
Sodium arsenite used	26·18	26·00	No satisfactory end-point	25·95
,, ,, ,,	26·00	25·95		25·95
.. .. ,,	26·10	25·95		25·97
Average ..	26·09	25·97		25·96

The calculated value of sodium arsenite solution required in all cases is 26·01 ml. The sodium arsenite used here was 0·0930 *N*. A litre of the thallic chloride solution was prepared from 12.2124 g. of thallous sulphate. The remarks made concerning the solutions under the titration by sodium thiosulphate apply here also.

The results show that this method is satisfactory down to concentrations of 0·002 *N* $TlCl_3$ with electrometric indicator, but only to 0·01 *N* with chloroform as indicator. At the latter concentration the end-point is a little delayed and rather difficult to define.

SUMMARY.—The bimetallic electrode system of Foulk and Bawden is satisfactory for the titration of iodine, liberated by thallic chloride from potassium iodide, with either sodium thiosulphate or sodium arsenite. Both reducing agents give good reproducible end-points with solutions of thallic salts of concentrations down to 0·002 *N*. In the case of sodium thiosulphate, the concentration of acetic acid may be varied between wide limits without affecting the end-point. The presence of zinc and ferrous iron has no effect on the titration value, but in the presence of copper, a titration value corresponding to the sum of the thallium and the copper is obtained. Consequently, the thallium may be determined in the presence of copper if the latter metal is subsequently determined by some other method.

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The Volumetric Determination of Nitrites by means of Ceric Sulphate Solution

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THE advantages of ceric sulphate solution as a volumetric oxidising agent in place of permanganate solution have been pointed out in recent years by a number of workers, and especially by Willard and Young,[1] Furman,[2] and Berry,[3] who have made use of standardised ceric sulphate solution for the determination of nitrites and many other oxidisable substances. In the present paper the direct titration of a nitrite with ceric sulphate has been examined, a dyestuff of the triphenylmethane class being used as internal indicator in the solution, and the procedure has been extended to include the indirect determination of the small amounts of potassium obtained in the analysis of soil solutions and similar materials, the potassium being precipitated with sodium cobaltinitrite and the washed precipitate titrated with ceric sulphate and ferrous sulphate solutions.

PREPARATION OF CERIC SULPHATE SOLUTION.—The ceric sulphate solution used for the experimental work was prepared (*a*) from technical ceric oxide and sulphuric acid, (*b*) from pure ceric ammonium nitrate by repeated evaporation with an excess of sulphuric acid.

The ceric sulphate solution was standardised against pure ferrous ammonium sulphate dissolved in air-free dilute sulphuric acid; the effect of atmospheric oxidation during the titration was found to be negligible. Erioglaucine was employed as internal indicator. 0·1 *N* ceric sulphate solution was used for the determination of the larger amounts of nitrite, 0·02 *N* solution for smaller amounts, and 0·01 *N* solution for the titration of the potassium cobaltinitrite precipitate. Solutions of ferrous sulphate of corresponding strengths were used in conjunction with the ceric sulphate solution.

The sodium nitrite ("Analar " B.D.H.) was dissolved in distilled water which had previously been boiled and cooled in a current of carbon dioxide to ensure freedom from air, and freshly-prepared solutions containing from 0·6 to 3·0 g. nitrite per l. were used for the determinations. The results were checked by parallel determinations with permanganate solution which had itself been standardised against sodium oxalate and ferrous ammonium sulphate, and figures in close agreement were obtained.

METHOD.—Twenty-five ml. of the standard nitrite solution were added to an excess of standard ceric sulphate solution containing a little 4 *N* sulphuric acid, the tip of the pipette being kept below the surface of the liquid during the addition. In some experiments the liquid was heated to boiling for one minute and then cooled; in others it was allowed to stand at the ordinary temperature for five minutes. In each case the excess of ceric sulphate was determined by titration with standard ferrous ammonium sulphate solution.

In the permanganate titrations the nitrite was added in the same way to a known volume of standard permanganate previously acidified with 5 ml. of dilute

(1 : 1) sulphuric acid, and the whole was slightly warmed. The liquid was well stirred and allowed to stand for a few minutes, after which an excess of sodium oxalate solution was added, and the whole was back-titrated with permanganate.

The following results are typical of the large number obtained:—

(*a*) Ceric sulphate solution, 0·195 *N* (1 ml. = 0·000673 g. of sodium nitrite).
50 ml. of ceric sulphate solution ≡ 48·8 ml. of ferrous ammonium sulphate solution.

Ceric sulphate ml.	Sodium nitrite added ml.	Ferrous solution used for back titration ml.
50	25	28·5
50	25	28·4

Ceric sulphate reduced ml.	Sodium nitrite in 25 ml. g.	Difference g.
20·80	0·140	—
20·69	0·139	−0·0001

(*b*) Permanganate solution, 0·0197 *N* (1 ml. ≡ 0·000681 g. of sodium nitrite).
15 ml. of sodium oxalate solution ≡ 7·63 ml. of permanganate solution.

Permanganate taken ml.	Sodium nitrite added ml.	Sodium oxalate added ml.
25	25	15
25	25	15

Permanganate for back titration ml.	Permanganate reduced ml.	Sodium nitrite in 25 ml. g.	Difference g.
3·1	20·47	0·139	−0·0001
3·2	20·57	0·140	—

In two of the series an excess of ferrous ammonium sulphate solution was added after the addition of the nitrite solution to the ceric sulphate, and the whole was back-titrated with ceric sulphate. In these experiments the results for sodium nitrite were usually a little higher (0·0001 to 0·0009 g.) than in the other tests, but were still quite satisfactory.

Determination of Potassium.—Preliminary experiments with a solution prepared from potassium sodium cobaltinitrite showed that reproducible results (*e.g.* 0·149, 0·147, 0·149 mg. in 5 ml.) were obtainable if the cobaltinitrite solution was added to an excess of 0·01 *N* ceric sulphate containing 3 ml. of 4 *N* sulphuric acid and the mixture was boiled for a minute. After cooling, 5 ml. of standard ferrous ammonium sulphate were added, and the excess was titrated with ceric sulphate, erioglaucine being used as indicator. With 0·01 *N* ceric sulphate the fading of the orange-pink colour after the end-point has been reached is more pronounced than with 0·02 *N* solution, but, despite this, the colour-change at the end-point is quite sharp.

A series of determinations was then made on a potassium chloride solution containing 0·1600 g. of the salt per l. The potassium was precipitated by the method used in the Agricultural Laboratory of this College. The potassium chloride solution was measured into a centrifuge tube and evaporated to 2 ml. Two drops of glacial acetic acid were added, and the tube was cooled in ice for 5 minutes, after which 0·75 ml. of sodium cobaltinitrite reagent was added slowly, the solutions being mixed by inclining the tube and then rapidly returning it to a vertical position. The tube was left in ice-water for 30 minutes and then centrifuged for 5 minutes, and the supernatant liquid was removed by means of a glass tube drawn out to a fine jet and attached to a suction-pump. The precipitate was washed twice with 2 ml. of water, the tube being centrifuged for 2 minutes at each washing. The precipitate was then washed into a 100-ml. beaker and dissolved by heating with 10 ml. of 0·01 *N* ceric sulphate and 4 ml. of 4 *N* sulphuric acid. The solution was cooled, 5 ml. of 0·02 *N* ferrous ammonium sulphate solution were added, and the excess of this was titrated with ceric sulphate after addition of erioglaucine as indicator.

Ceric sulphate solution, 0·00992 *N*. 1 ml. ≡ 0·0705 mg. potassium. The ceric sulphate solution was standardised with ferrous ammonium sulphate. The following results are typical:—

Potassium solution ml.		chloride taken mg.	Ceric sulphate reduced ml.	Potassium found mg.	Difference mg.
2	=	0·168	2·43	0·171	+0·003
2	=	0·168	2·45	0·173	+0·005
7	=	0·587	8·87	0·625	+0·038
7	=	0·587	8·96	0·632	+0·045

A comparative series of determinations in which the cobaltinitrite precipitate was titrated with permanganate solution also gave results that were quite satisfactory for small amounts of potassium (0·17 to 0·40 mg.), but tended to become irregular with larger amounts.

In two series of experiments, in which the potassium was precipitated with Kramer's solution (a solution of cobaltinitrite made from cobalt nitrate and sodium nitrite), the results were invariably higher than when a precipitant prepared from solid sodium cobaltinitrite was used. It is evident that the composition of the precipitate varies with the conditions of precipitation and the composition of the reagents used. In several of the series it was possible to calculate for the ceric sulphate a potassium factor which afforded satisfactory values throughout the whole range of that particular series, but could not be used for any other series of determinations made under even slightly differing conditions.

Considered as a whole, our results confirm those of previous workers when using permanganate solution in the titration of the cobaltinitrite precipitate,[4] and clearly indicate that accurate determinations of these small amounts of potassium can be attained only by rigid control of the conditions of precipitation and filtration, and by standardising the permanganate or ceric sulphate solutions against a solution of pure potassium chloride treated in exactly the same way as in the actual determination.

The method finally recommended for the titration of the cobaltinitrite precipitate is as follows:—The washed precipitate is dissolved by heating it with 10 ml. of 0·01 *N* ceric sulphate solution and 4 ml. of 4 *N* sulphuric acid. Five ml. of standardised ferrous sulphate solution are added to the cooled solution, and the excess of the ferrous solution is titrated with the ceric sulphate solution. This procedure has the advantage of avoiding danger of decomposition of the standard solution in the hot liquid, which is the drawback of the customary permanganate method.

SUMMARY.—Soluble nitrites may be accurately determined by titration of their solutions with ceric sulphate solution, erioglaucine being employed as internal indicator.

In the determination of small amounts of potassium in soil solutions, etc., by the cobaltinitrite method, ceric sulphate may advantageously replace permanganate in the titration of the potassium cobaltinitrite precipitate.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

CURVES FOR USE IN THE COLORIMETRIC ESTIMATION OF CAROTENE

THE colorimetric estimation of carotene has been carried out for many years by comparison with potassium dichromate solution. Many workers have prepared crystalline carotene and with its help constructed curves, potassium dichromate of varying strengths being used for matching. While this may be satisfactory when the worker is engaged in experiments in which relative carotene-contents are examined, variation in the purity of the samples of carotene used for the construction of the curves may lead to conflicting results when comparative work on absolute amounts of carotene is carried out by several workers.

It was decided to construct a curve with highly purified carotene, which might act as a standard for future work, the Lovibond Tintometer (B.D.H. Pattern) being used for the purpose. At the same time a comparison was made against the usual potassium dichromate solution.

Several samples of carotene were examined, but one, for which I am indebted to Professor A. C. Chibnall and Dr. A. Pollard, of the Imperial College of Science and Technology, was of outstanding purity.

This carotene,* prepared from cocksfoot grass (*Dactylis glomerata*), was entirely in the β-form, and its melting-point was 180–182° C. (182° corr.).

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* The carotene was isolated during an extensive fractionation of all the ether-soluble material from cocksfoot (*Dactylis glomerata*). Details will be published later.

The intensity of absorption of light at $463 m\mu$ was taken as the criterion of purity. Mr. A. E. Gillam, of Manchester University, kindly made the spectroscopic examination. He reports the sample to be the purest he has met with. The absorption data in chloroform were as follows:

$E^{1\%}_{1\,\text{cm.}}$ $(463 m\mu) = 2200$,* where $E = \log \frac{I_0}{I}$, I_0 = the intensity of incident light, and I = the intensity of transmitted light in a cell 1 cm. in thickness.

Expressed as the molar extinction coefficient, E_1, this equals 118,000 $[E_1 = \log \frac{I_0}{I} \div$ (molar concentration $\times$ cell thickness in cm.)].

This sample was used for the construction of the curves; 10·15 mg. were dissolved in about 20 ml. of chloroform, and the volume was made up to 500 ml. with petroleum spirit (b.p. 40°–60° C.). From this solution seventeen dilute solutions were prepared by dilution with petroleum spirit and matched in the Lovibond Tintometer, daylight from a north window being used as the source of light. Readings were made by three independent observers, and the results were averaged. The individual readings usually lay within 0·1 unit, but a maximum difference of 0·4 unit was obtained with two of the more concentrated solutions. To obtain perfect matching, it was necessary to make use of the red slides in amounts varying from 0·2 unit in the more dilute solutions to 0·5 unit in the strongest solutions. These amounts are small, and only the yellow units were used for the curve.

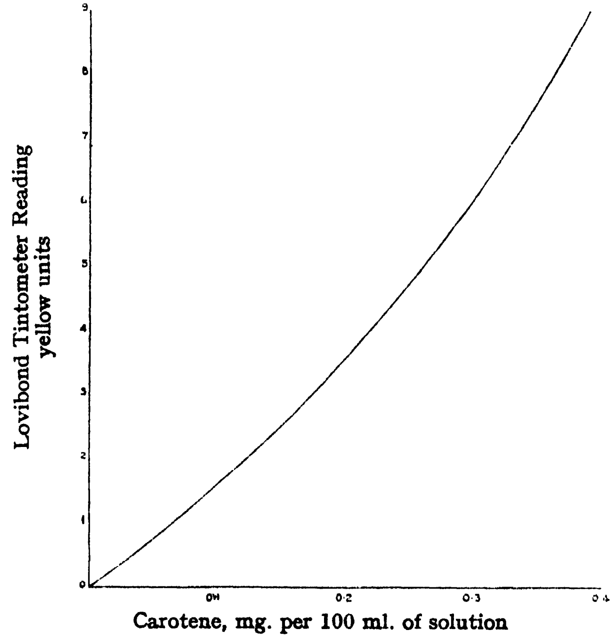

Fig. 1

The curve is shown in Fig. 1. The values go no higher than 9 Lovibond yellow units, owing to the difficulty of matching accurately above that density;

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* The highest value Mr. Gillam had obtained previously in his wide experience was $E^{1\%}_{1\,\text{cm.}}$ $463 m\mu = 2000$.

experience has shown that the most accurate values are obtained when the colours lie within the range of 2 and 5 yellow units.

Potassium Dichromate Solution as Standard.—From a freshly-prepared carotene solution ten further dilute carotene solutions were made up, and these were compared against 0·1 per cent. potassium dichromate solution in a Klett colorimeter, the source of light being north, as before.

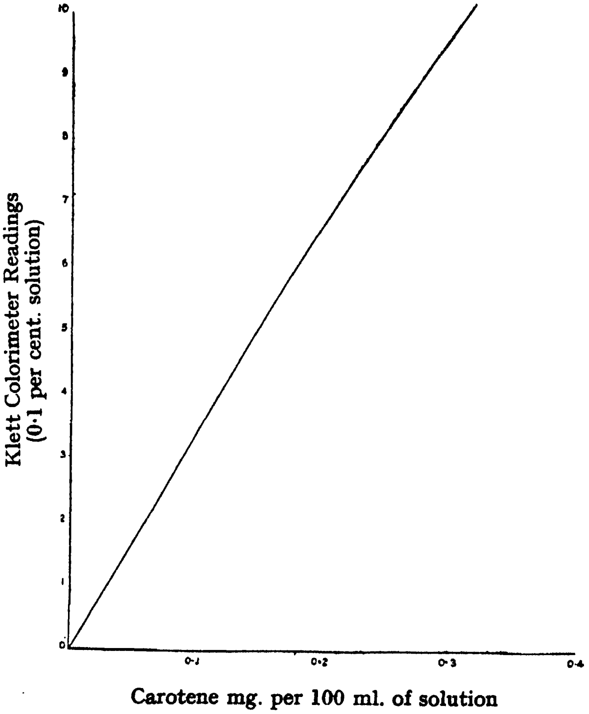

Fig. 2

The carotene solutions were set at 20 mm. on the scale, and the matching was done by varying the height of the potassium dichromate column. This method has

Table I

Data for Construction of Curve (Tintometer)

Carotene per 100 ml. mg.	Tintometer reading, yellow units	Carotene per 100 ml. mg.	Tintometer reading, yellow units
0·0609	0·95	0·2436	4·55
0·0812	1·30	0·2639	5·00
0·1015	1·60	0·2842	5·70
0·1218	2·05	0·3045	6·10
0·1421	2·30	0·3248	6·90
0·1624	2·80	0·3451	7·35
0·1827	3·20	0·3654	8·05
0·2030	3·70	0·3857	8·75
0·2233	4·05		

been found very convenient, and it has given satisfactory results in a number of comparative tests with the Lovibond tintometer method.

The curve is shown in Fig. II. It was again found that the matching was easier and more accurate at the lower concentrations.

To enable workers to construct their own curves on a larger scale than that published here, the actual figures obtained in the work are given in Tables I and II.

TABLE II

DATA FOR CONSTRUCTION OF CURVE (KLETT COLORIMETER)

Carotene per 100 ml. mg.	Depth of 0·1 per cent. $K_2Cr_2O_7$ column, mm.	Carotene per 100 ml. mg.	Depth of 0·1 per cent. $K_2Cr_2O_7$ column, mm.
0·0483	1·60	0·1800	6·04
0·0676	2·26	0·2029	6·85
0·0966	3·21	0·2318	7·65
0·1256	4·19	0·2705	8·79
0·1546	5·16	0·3280	10·50

My thanks are due to Mr. E. Sampson and Mr. F. Reed for assistance in the colour matchings and to Messrs. Imperial Chemical Industries, Ltd., for permission to publish this note.

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TIN AND LEAD IN CANNED FISH

ONE hundred and forty-six samples, mostly purchased at random, and comprising about 100 different brands of various kinds of canned fish, have been examined recently for metallic contamination by Mr. H. G. Harrison and myself; 20 were reported upon adversely, the results being summarised below:

Sardines.—Of 28 samples analysed, none contained more than small amounts of tin, but 10 contained lead in excess of 7 parts per million, *viz.* 8, 9, 10, 10, 15, 15, 16, 20, 21, and 43 p.p.m., respectively.

In determining the lead in canned fish it was found that the direct colorimetric method on the clear solution obtained by the acid-destruction of 5 g. of the thoroughly mixed sample, with the use of appropriate reagents to prevent interference from iron, copper, phosphates, etc. (Lampitt and Rooke, ANALYST, 1933, **58**, 736), gave results closely agreeing with those given by the diphenylthiocarbazone method of Allport and Skrimshire (ANALYST, 1932, **57**, 443), and the former method would appear to be satisfactory for general routine, provided that colourless solutions are obtained.

The sardines containing the higher proportions of lead were all packed in Portugal, and the cans showed no obvious signs of corrosion or exposed solder; the explanation of the contamination doubtless lies in the Portuguese method of steam-cooking on lead-containing grills, as explained by Lampitt and Rooke (*loc. cit.*).

A further point of interest was that two samples, sold as sardines, bore unusual markings and were accordingly submitted to further examination to establish their identity. The pieces of fish submitted were more slender in shape, lighter in colour, and less scaly than sardines; a long dorsal fin extending almost to the tail and long pointed pectoral fins were observed on dissection, but the most characteristic features were pronounced spiny projections all along the lateral line, and a sharp curve downward in the middle of this line. From information obtained at the Fishmongers' Hall, and by comparison with specimens with Mr. J. R. Norman's kind assistance at the Natural History Museum, it was definitely established, even in the absence of their heads and tails, that the fish belonged to a species of *Trachurus*, a horse mackerel or scad (family, *Carangidae*), a fish of different natural order from the sardine, and far inferior in flavour and value.

In fairness to the packers it should be stated that both samples proved to be of the same brand and to be sold in tins labelled "Portuguese Fish in Oil." Nothing can be said at the time of writing as to the value of this declaration as a defence for the vendor.

Brisling, etc.—Eight samples of brisling in oil, 7 of pilchards in tomato sauce, 15 of herrings in tomato sauce, 10 of crab, 4 of salmon, 2 of lobster, 1 of oysters and 1 of mackerel, were all free from more than traces of lead or tin. It appears that the distinction between sardines and pilchards and between sild and herring is merely one of size (*cf.* Hattersley, ANALYST, 1935, 69).

Sild.—Seventy samples of tinned sild showed no excessive amounts of lead; 12 samples, however, contained more than 2 grains of tin per pound, the results being as follows:

Tin-content in grains per pound	Number of samples
Less than 1	41
From 1 to 1·9	15
„ 2 to 2·9	4
„ 3 to 3·9	4
„ 4 to 6·7	5

The tin was determined by the gravimetric method of Buchanan and Schryver (L.G.B. Report, No. 7, 1908; Abst., ANALYST, 1909, **34**, 121). It may be of interest to mention here that quantities of tin approaching and exceeding 2 grains per lb. can usually be detected visually by the yellowness of the ash when hot; also, that the ignited sulphide precipitate from a hydrochloric acid extract of the ash, determined in 20 cases in an attempt to find an expeditious method, gave from two-thirds to three-quarters of the tin found by the former method. A volumetric process involving an iodimetric titration of the stannous chloride formed by the reduction by aluminium wire of the hydrochloric extract from the ash, in an atmosphere of carbon dioxide, proved quite unreliable, no doubt on account of incomplete solution of the tin and interference by iron, etc.

Of the samples containing excessive amounts of tin, one (tin, 2·6 grains per lb.) was stated to be British and contained tomato sauce, which might have accounted for some corrosion, whilst the remainder were cheap brands of Norwegian origin. It was observed that in most of the latter the oil used was not olive oil, and appeared to be deficient in quantity; this may account for the presence of tin, for the cans, although evidently not from old stock, showed marked signs of corrosion in patches where the fish had been in contact with the sides, suggesting that the oil was insufficient in quantity to protect the tin from the action of the salts, etc., in the fish. Indeed, three corroded cans contained scarcely any oil.

In most of these cases of metallic contamination appropriate action taken by the authorities concerned has prevented the further sale or importation of such consignments, thus avoiding the necessity for actual prosecutions.

A Suggested Standard for Lead in Canned Fish.—While it is obvious that the contamination of fish intended for human consumption with a poisonous metal, such as lead, should be entirely prevented, it is necessary to choose a certain degree of contamination to serve as a limit for practical administrative purposes.

It is very desirable that the same limit should be adopted in all districts, and in the absence of a legal or authoritative ruling, I venture to suggest that one-tenth of a grain of lead per pound might be generally adopted as a maximum limit, pending the promulgation of an official or semi-official standard. This figure is equal to approximately 14 parts per million. There seems to be no reason why the proportion of lead in tinned fish could not be kept well within such a figure and, this being about twenty times that generally regarded as dangerous for drinking water and over ten times the proportion found in cider responsible for the 1932 outbreak of lead poisoning (*Lancet*, 1932, **223**, 717), it can hardly be regarded as a stringent limit, and would only exclude definitely contaminated fish. On the other hand, the universal enforcement, at this stage, of a materially lower limit would apparently prove extremely difficult and likely to cause considerable hardship.

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ANALYSIS OF TURPENTINE LINIMENT

Evers and Elsdon, in "The Analysis of Drugs and Chemicals," state that the turpentine and camphor in this liniment may be determined together by distilling 50 g. of the liniment with steam. In practice, it has been found difficult to control frothing, but the addition of 0·5 ml. of syrupy phosphoric acid breaks the emulsion and prevents the trouble. The distillation may then be carried out much more rapidly. Identical results are obtained by the two methods.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF LEEDS

Annual Report of the City Analyst for the Year 1934

Labelling of Lard Substitutes.—An imitation vegetable substitute, prepared by hardening cotton-seed oil, was sold as lard. The shopkeeper's explanation was that all her customers knew that they were receiving, not lard, but "lardine." She was subsequently warned by the Medical Officer of Health that in future this commodity must be suitably labelled. In view of the quantity of lard substitutes now on the market, it seems most desirable that they should be required by law to be sold in wrappers distinctively labelled in letters of a specified size, so that the same distinction may be made between lard and its substitutes as is now made between butter and margarine.

Flavouring Essences.—On account of questions asked in the House of Commons in December, 1933, regarding flavouring essences, informal samples of rum, raspberry, and lemon essences from a local store were submitted for analysis and found to contain 70, 30 and 35 per cent. of isopropyl alcohol, respectively. No excise licence is needed, and the only requirement relating to the use of isopropyl alcohol is that, according to the Isopropyl Alcohol Regulations, 1927, manufacturers and sellers must make a six-monthly return to the Excise Authorities of the quantities used. Hence, this alcohol has recently been widely used both for perfumery and culinary flavours, with material falls in the prices of the articles. Isopropyl alcohol is stated to be safe for internal use in small doses in dilute form, and to be a solvent that might be used for making tinctures.

CAMPHORATED OIL.—A sample was found to contain 19·3 per cent. of camphor and 80·7 per cent. of olive oil, instead of the 20 per cent. of camphor required by the B.P., 1932. This sample was interesting from the fact that advantage had been taken of the permission given in the B.P., 1932, to use artificial camphor for the preparation of this liniment.

IDENTIFICATION OF FACE POWDER.—In the case of *Rex* v. *Blake*, tried at the West Riding Assizes in December, 1934, the prisoner was convicted of the murder of a woman. Certain powders were analysed in connection with the case, one of them being a face powder contained in a "Phul-Nana" powder box found in the prisoner's possession and identified as the dead woman's property by the shape of a tear on the lid. The defence having submitted that the box and powder belonged to the prisoner's wife, who stated that she had mixed some white Yardley compact with the "Phul-Nana" powder in her box, evidence was given to the effect that the white lumps in the box were not those of another face powder, but consisted of boric acid, which constituted 85 per cent. of the mixture. Neither of the face powders mentioned contains boric acid.

C. H. MANLEY

CITY OF LEICESTER

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1934

DYED SUGAR.—A sample was submitted under Sec. 17 (2) of the Food and Drugs (Adulteration) Act, 1928, because of its green appearance after wetting, especially when the wetting medium was milk. The trouble was found to be due to a film of spirit-soluble dye on the surface of the crystals.

STERILISED MILK.—The standard, adopted some years ago, of a maximum count of 1000 organisms per ml., seems fair, and most supplies comply with it. Four of 16 samples failed to reach this standard, and one had a count of 570,000 per ml.

BATH WATERS.—The following standards and system of sampling, adopted early in 1932 for indoor swimming baths, have been found workable:

Standards.—(i) The free chlorine shall not exceed 0·5 part per million.

(ii) The total number of colonies developing in 24 hours on nutrient agar at blood heat shall not exceed 1000 per ml.

(iii) *Bacillus coli* shall not be present in more than two out of five 10-ml. tubes.

System of Sampling.—Each bath is sampled the first week it is open to the public for the year. If the water fails to comply with any one of the above tests, it is sampled again weekly until a satisfactory sample is obtained. It is then sampled again after a fortnight, and, if still satisfactory, it is sampled thereafter once a month. If the first sample from a bath is satisfactory, it is sampled again after a fortnight, and thereafter monthly while it remains satisfactory. It thus follows that the number of samples required to be taken is inversely as the quality of the water; and the drop in the number of samples taken in 1934 is explained.

A large privately-owned open-air swimming pool was opened to the public in the summer just inside the City boundary at Knighton. Up-to-date filtration and chlorinating plant was installed, but, for some reason, was not put into commission. Consequently the water failed to reach the necessary bacterial standards. It is expected that this will be remedied in 1935.

SUSSEX GROUND OATS.—Three samples, taken informally under the Fertilisers and Feeding Stuffs Act, 1926, contained excessive amounts of fibrous material.

The maximum amount of fibre likely to occur in genuine Sussex ground oats is 12 per cent., whereas these three samples contained, respectively, 15·4 per cent., 15·4 per cent. and 17·3 per cent. No declaration of fibre-content is required under the Act for Sussex ground oat samples, but added husks or glumes have to be declared. It was not possible to state conclusively whether the high fibre was due to grinding very thin oats, or whether extraneous husk had been added, but the figures obtained raised a very strong presumption that the latter was the case.

SULPHUR IMPURITIES IN THE ATMOSPHERE.—The relatively simple method of the Building Research Station for measuring sulphur gases in the atmosphere was tried throughout the year and found to have many advantages. Briefly, it consists in exposing a cylinder, of known superficial area, covered with an absorbent surface of lead peroxide, to the atmosphere for a definite period, and then determining the amount of lead sulphate formed by absorption of the sulphur gases (*cf.* ANALYST, 1933, **58**, 284). The amounts of sulphur dioxide found in the atmosphere by the volumetric method developed in the Government Laboratory were as follows:—January (average), 17·0; February (foggy), 109·0; (fog clearing) 64·0; (warm, bright, clear) 15·0; May (fine, sunny), 4·0; October (average), 12·0; (night reading), 6·0; November (average), 17 parts per 100,000,000.

"SPECIAL COFFEE."—Three samples of coffee from a stall were sent in by the Chief Constable. One shilling per cup was charged for this "special" line, instead of the usual twopence. Rum was found in each sample, and the vendor was convicted for selling intoxicating liquor by retail without having a Justices' licence.

F. C. BULLOCK

Department of Scientific and Industrial Research

REPORT OF THE FOOD INVESTIGATION BOARD FOR 1934*

THE Report of the Food Investigation Board aims at presenting a concise statement of the progress of the investigations carried out during the year 1934. The results of the investigations are published in full from time to time on completion. The arrangement of the Report differs from that of previous years, the various investigations being grouped according to subject-matter instead of under the names of the laboratories concerned.

SECTION I. MEAT.—The experiments on the storing of chilled meat in air enriched with carbon dioxide have resulted in the carrying of 4400 tons of chilled beef from Australia and New Zealand during 1934. The problem of gas leakage now appears capable of practical solution, but a number of problems connected with the proper conditions of cooling, humidity and air circulation for preservation to the fullest possible extent of the natural appearance of the meat are still being investigated.

In connection with palatability of meat, methods for determining the amounts of individual proteins have advanced sufficiently to permit of such changes as denaturation being followed with some certainty. Ozone has been found to be germicidal to bacteria in concentrations of the order of 100 to 1000 parts per million, whilst the mortality of bacteria rapidly frozen in solid carbon dioxide is greatest at 0° to −5° C. Work has been carried out on the use of non-toxic anti-oxidants, *e.g.* sodium citrate, sodium malonate and glycine, in connection with the preservation of edible fats.

SECTION II. EGGS.—A preliminary study of the changes taking place when eggs are stored in air and in air enriched with carbon dioxide shows that, in order to maintain the pH of the white at 7·9, eggs must be stored in atmospheres containing approximately 10 per cent. of carbon dioxide at 20° C., or 3 per cent. at 0° C. The strength of the membrane enclosing the yolk is an important factor in the preservation of eggs, and the average thickness is about 64/100,000 of an inch, and in a fresh egg its bursting strength is about 0·065 lb. per sq. in. This falls on storage, and, when it is only a little over half the strength, the yolk breaks easily. The whites of eggs were found to be sterile, except those of a few imported eggs, whilst the yolks tended to be sterile or nearly so in July, but had a larger bacterial count in September.

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* **H.M. Stationery Office, Adastral House, Kingsway, W.C.2. 1935. Price 4s. net.**

SECTION III. PORK, BACON AND HAMS.—An investigation, in collaboration with the Cambridge School of Agriculture, has been started, of the factors affecting the quality of the pig carcase, and it has been already shown that fat sides lose slightly less weight during maturation than lean sides. A new method for determining the distribution of fat in lean meat is to measure the electrical resistance of the meat, since the resistance of the fat is several times greater than that of the lean. It has been found that by using an atmosphere of carbon dioxide at a temperature of 5° C., at least 3 weeks can be added to the storage life of mild-cured bacon.

SECTION IV. FISH.—Much work has been done in connection with the herring industries. Herrings that had been brine-frozen at the usual temperature of −5° F. made good kippers after at least 5 months' storage, and experiments under commercial conditions are being conducted. The metabolism of fats in fish has continued to receive attention. Marked specific resemblances have been found between fats of fresh-water algae and zooplankton and those of fresh-water fish, in contrast with corresponding resemblances between those from marine sources. The fats of the porpoise and dolphin have received particular attention. In the study of the transport of fish it has been found that a saving of ice may be effected by the use of vegetable parchment paper enclosing the mass of fish and ice in the box, owing to the protection afforded against currents of air.

SECTION V. FRUIT AND VEGETABLES.—Only a few of the many investigations under this heading can be mentioned. The trials of English varieties of apples in gas storage have shown that for most varieties an atmosphere containing 5 per cent. of carbon dioxide and 2·5 to 5 per cent. of oxygen is best, and a table is published showing recommended temperatures and atmospheres for 8 culinary and 6 dessert varieties. One result of the further study of the critical changes occurring at the climacteric in the apple is the identification of ethylene as the active substance that is given off by apples at this point; this substance also stimulates this change in other apples. It has been established that, prior to the development of the disease known as "low-temperature breakdown," the amino acids reach a maximum concentration in the tissues, owing to a change in the relative proportions of the components of that fraction of the nitrogenous constituents which is soluble in alcohol.

In connection with the rotting of fruit in storage it has been found that wraps treated with iodine retard the development of fungal rotting in various types of fruit without impairing the appearance or flavour, or hastening ripening (*J. Pomol.*, 1934, **12**, 311). Grapes, tomatoes and oranges all showed marked improvement, as also did certain varieties of plums and peaches, but other varieties failed to ripen properly, and some even turned brown. Papers may be soaked in a solution containing 12·7 g. of iodine, 10·0 g. of potassium iodide, 200 ml. of water, and 800 ml. of rectified spirit. At a temperature of 15° C., tomatoes in plain papers developed mould in 38 days, but those in iodised papers required 72 days. Experiments are now being carried out on a commercial scale. This method cannot be applied to the storage of prepared foods or meat.

In the study of the stored-apple diseases it has been shown that "scalding" results from changes in the tissues occurring weeks or months before the injury is apparent, and that prevention by oiled paper wrappings is efficient chiefly during these early stages. Scald is regarded as due to an excessive accumulation of some volatile substance in the tissues.

The vitamin *C* content of apples, which is known to increase as the skin is approached from the core, has been found to vary in the red and green peel of Bramley Seedling apples. Red peel was found to be more than twice as active as regards vitamin *C* as green peel, although no difference could be found in the activities of the pulps. Storage of Bramley Seedling apples from mid-September to mid-December in pure oxygen and pure nitrogen (less than 0·5 per cent. of oxygen) in containers continuously ventilated with these gases at 1° C. had no effect on their vitamin *C* potency.

SECTION VI. CANNING.—Synthetic vitamin *C*, which is now known to be identical in chemical structure and in biological activity with the natural vitamin, added to such foods as runner beans, apples or apple jelly, remained substantially stable during the canning, and the loss was in no case greater than 25 per cent. Antiscorbutically-active products may thus be obtained equal to such natural sources of vitamin *C* as the citrus fruits.

Tests with plain and lacquered aluminium cans and the principal English fruits go to show that plain and once-lacquered cans are unsatisfactory, and that aluminium is even more dependent than tinplate on the protection the lacquer affords. Work on the diffusion of hydrogen through mild steel sheet and tinplate shows that hydrogen evolved during corrosion can diffuse comparatively rapidly through steel, and, to some extent, through tinplate. The rate of diffusion varies with different steels, and is affected by addition of substances known to accelerate or inhibit acid corrosion. The diffusing hydrogen appears to be in a specially active state, probably atomic. The changes in the setting value of the pectin in fruits during storage have been further studied, and a table is given summarising the changes for raspberries, gooseberries and apples.

SECTION VII. ENGINEERING.—The influence on the relative humidity in cold stores of the heat produced by the stored material has been studied in detail, and since heat leaking in from outside exerts similar effects, a jacketed construction has been proposed for cold stores where high relative humidities are required. A new method of cooling ships' holds, suitable for a large range of cargoes, has been suggested; it involves a two-stage system of air circulation, the air-stream passing vertically down through the cargo and returning to the cooler by way of a jacket, lining the sides, in which the heat of leakage is removed. The method is being adopted in some of the new steamers, with modifications according to the particular cargo.

D. G. H.

Alkali &c. Works

ANNUAL REPORT OF THE CHIEF INSPECTORS FOR THE YEAR 1934*

THIS is the 71st Annual Report of the Chief Inspectors under the Alkali etc. Works Regulation Act, and the Alkali etc. Works Order, 1928, to the Minister of Health, and to the Department of Health for Scotland. For the first time since 1917 there has been an increase in the number of works registered over that of the previous year. The number of works registered in 1934 was 918, involving the operation of 1759 separate processes.

A draft Order† was prepared by which it is proposed to add to the list of noxious or offensive gases:

(1) Fumes containing silicon, calcium or their compounds.

(2) Fumes from paraffin oil works containing any sulphur compound.

It is proposed, further, to extend the list of scheduled works to include "Cement Production Works" (under a new definition) and to widen the definitions of muriatic acid works (*a*), bisulphide of carbon works and paraffin oil works.

As in previous years, much of the District Inspectors' time has been occupied by visits and inquiries in connection with unregistered processes.

The number of cases in which statutory limits of acidity tolerated by the Act have been exceeded, or in which other infringements have occurred, was less than in the previous year, and no case was sufficiently serious for legal proceedings to be taken.

There is no doubt that the public is more concerned than ever about air cleanliness, as regards pollution both by smoke and by dust, as well as by offensive gases. Local authorities, too, have frequently appealed to the Ministry for advice and assistance in dealing with difficult problems.

FUMES FROM WIRE ENAMELLING.—The characteristic harshness of these fumes is probably due to acroleinic substances and hydrocarbons. Complaints have been reduced by re-designing the drying stoves and by an improved system of draughting.

POWER STATIONS.—Regular determinations have been made of the sulphur oxides content of waste gases emitted from the stacks of the Battersea Power Station. The washing plant installed at the station has operated continuously and efficiently. The acidity of the chimney gases has been satisfactorily low, and there has been an almost complete absence of smoke.

Determination of Sulphur Oxides in Chimney Gases.—The method used for the determination of sulphur oxides in the chimney gases was as follows:

A 120-ml. Dreschel wash bottle, fitted with a sintered glass septum 2 cm. in diameter, sealed to the inlet tube, was used as an absorber. Twenty ml. of 10-vol. hydrogen peroxide and 50 ml. of water were placed in the Dreschel bottle, and a similar amount retained for a blank determination. Gas was drawn from the chimney through the absorber and a meter by means of a pump at a rate of about 1½ cb. ft. per hour. (The Dreschel bottle and solution offers a resistance equivalent to 12-in. water pressure.) When about 2 cb. ft. of gas had been washed the pump was stopped, the meter read, and the solution from the washer was transferred to a titrating flask. The acidity or alkalinity of the blank was determined by titration with $N/20$ acid or alkali. The sample was then similarly titrated, the blank being used as a standard for colour.

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* Report by Dr. W. A. Damon and Dr. B. Wylam, pp. 44. H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. 1935. Price 9d. net.

† The Order (Statutory Rules and Orders, 1935, No. 162) came into operation on April 1st, 1935.

By a long series of experiments it has been proved that this method is reliable. The presence of carbon dioxide has no effect on the absorption, and the oxidation of sulphurous to sulphuric acid appears to be instantaneous.

Pulverised Fuel.—The use of pulverised fuel makes the employment of dust-arrestment plant imperative if falling dust in the atmosphere is to be avoided. With a high chimney it is improbable that any inconvenience would be caused at ground level by sulphurous fumes, but a chimney, however tall, does not lessen atmospheric pollution.

ALKALI AND COPPER (WET PROCESS) WORKS.—The average escape of hydrochloric acid gas into the atmosphere has been satisfactorily low (0·069 grain HCl per cb. foot). The question of the 95 per cent. condensation figure required by the Act was discussed in the 68th Report. Since then manufacturers have been asked to make returns of salt used and acid produced, and efficiencies have been calculated from those figures. These show considerable variation. It is realised, of course, that a figure based on such data is not necessarily the same as a condensation figure, because there may have been leakages and other losses of condensed acid; nevertheless, it is a useful figure on which to base comparisons.

The moisture and purity of the salt used vary at different works, as also does the proportion of undecomposed chloride in the salt-cake. Taking a round figure of 90 per cent. for the sodium chloride-content of the salt and ignoring that in the salt-cake, the average efficiency for all salt-cake processes works out at 94·1 per cent. Individual results vary from 83·5 per cent. to 104·6 per cent., showing that there is room for much improvement at some works.

FUMES FROM A COPPER REFINERY.—In the investigation of a complaint, the method of estimating atmospheric pollution devised by the Building Research Station has been used (*cf.* ANALYST, 1933, **58**, 284). The results up to date are somewhat inconclusive, but they certainly have afforded no definite evidence that the locality from which many complaints emanated is suffering from the fumes.

SULPHURIC ACID WORKS.—The production of sulphuric acid in England and Wales during 1934 was 730,000 tons—an increase of 81,500 tons compared with the production in 1933.

Determination of Total Acidity of Chamber-Plant Escapes.—The method of testing hitherto employed by District Inspectors is unsatisfactory, since it does not include all the acidity due to the oxides of nitrogen. The following modified test (described in Appendix V) has therefore been devised, and, should it prove satisfactory in practice, it is proposed to adopt it as the official method. Section 6 (1) of the Act distinctly provides that "the acid gases of sulphur or of sulphur and nitrogen . . . shall not exceed the equivalent of 4 grains of sulphuric anhydride."

A Winchester quart of known capacity is fitted with an aspirator attachment consisting of an inlet and outlet tube of glass tubing, 1 cm. in diameter. The bottle is dried by means of alcohol and ether, and a sealed tube containing 10 ml. of 10-vol. hydrogen peroxide is placed in it. The inlet-tube, *i.e.* the one reaching to the bottom of the bottle, is connected with the sampling tube, and the outlet with a Fletcher's bellows. Four aspirations are made to ensure replacement of air in the bottle by exit gas, and the inlet and outlet are then closed by clips and disconnected. The bottle is shaken to break the tube of peroxide and to wet the walls. It is allowed to lie on its side for 20 minutes with occasional shaking, and the contents are then washed out into a basin. Ten ml. of $N/10$ caustic soda are added, and the excess is determined by back-titration with $N/10$ acid, methyl red being used as indicator.

Should there be any sign of entrained acid in the exit gases, the inlet-tube should be fitted with a plug of glass wool. This may be washed and the washings titrated separately, one-fourth of the acidity being added to the figure obtained for acidity of the gas contained in the bottle.

Such tests as have already been made indicate that a normal escape of from 1 to 2 grains of sulphur dioxide is usually accompanied by 0·5 to 1 grain of oxides of nitrogen (expressed as NO_2). It will be found that this amount of escape corresponds roughly with a nitre-consumption figure of 3 lbs. $NaNO_3$ per 100 lbs. of sulphur burned, so that there are some grounds for thinking that the loss of nitre viâ the exit very nearly balances that supplied (as make-up) to the plant.

Manufacturers would do well to introduce the modified method of testing at their works, either instead of, or in addition to, the ordinary quick test. Not only does it give a truer estimate of acidity, but it also affords an indication of the loss of nitre.

Sulphuric Acid as a Spray for Cereal Crops.—The use of sulphuric acid for spraying cereal crops to kill charlock and other annual weeds has been extended; the sales of acid for this purpose have been quadrupled, compared with those of the previous year.

CHLORINE.—The use of chlorine in industry is expanding, and a number of new works have been registered.

The application of chlorine for the purpose of slowing down the rate of decomposition has lately been practised at a certain sewage works. The chlorine cylinders are housed in structures which are situated in the public road, but they are protected against impact by steel barriers. It is understood that the process is experimental, and that, if successful, the cylinders will be housed in underground structures.

To avoid corrosion of chlorine feed-pipes in the manufacture of calcium hypochlorite, various materials have been tried. Of these, tellurium lead (*cf.* ANALYST, **1933**, **58**, 367) has offered the greatest promise, but most manufacturers still prefer to use pipes of mild steel or wrought iron and to renew them frequently.

CARBON DISULPHIDE WORKS.—Recovery from the sodium methyl xanthate is practised at only a few works. Some difficulty has been experienced in disposal of the recovered material, and fears are entertained lest the excessively foul gases liberated in the process may occasion trouble.

An investigation (detailed in Appendix IV) indicates that an alkaline xanthate on storage breaks down to sulphide and carbonate. On acidification, therefore, the quantity of hydrogen sulphide liberated increases with the age of the xanthate, while the recoverable carbon disulphide decreases. A neutral xanthate is more stable, but exhibits a tendency towards production of the even more objectionable mercaptans. Clearly, every precaution should be taken to deal with gaseous emissions from this process. There is no insuperable difficulty in doing so, as has been demonstrated at two works where the process has been operated without any offence during the past year.

Milk Act, 1934

[24 & 25 GEO. 5, CH. 51]*

AN Act to provide for temporarily securing to producers of milk, by means of payments out of moneys provided by Parliament, a minimum return in respect of milk used in the manufacture of milk products; for conditionally requiring repayment to the Exchequer of the amount of such payments; for making, out of moneys so provided, payments for the purposes of improving the quality of the milk supply and increasing the demand for milk; for regulating the manner in which milk is described for the purposes of advertisement and sale; for imposing and conferring certain duties and powers on boards administering milk marketing schemes; and for purposes connected with the matters aforesaid. [31st July, 1934.]

The arrangement of the sections of the Act is as follows:

Payments from and to the Exchequer in respect of milk used for manufacture.
Section
1. Exchequer payments in respect of milk sold for manufacture.
2. Exchequer payments in respect of milk used for manufacture by milk marketing boards.
3. Exchequer payments in respect of milk converted into cheese at farms.
4. Definition of "cheese-milk price" and "standard price" and certification of cheese-milk price.
5. Payments to Exchequer in respect of milk used in manufacturing milk products.
6. Exchequer payments to Government of Northern Ireland in respect of milk used for manufacture.
7. Provisions for enforcing payments due to Exchequer.
8. Provisions as to revocation of schemes.

Provisions for improving the quality of the milk supply.
9. Payments for securing pure milk supply.
10. Amendment of 12 & 13 Geo. 5, c. 54.

Provisions for increasing the demand for milk.
11. Contributions from Exchequer towards expenses of milk marketing boards.

General and supplementary provisions.
12. Extension of functions of milk marketing boards.
13. Interpretation.
14. Short title and commencement.

Section 10 provides that the following section shall have effect in substitution of sec. 3 of the Milk and Dairies (Amendment) Act, 1922:

"3.—(1) The Minister of Health, after consultation with the Minister of Agriculture and Fisheries, may by order—

(*a*) prescribe, in relation to milk of any description, such designation (hereinafter referred to as a 'special designation') as he considers appropriate; and

(*b*) as respects any special designation, provide for the granting by the Minister of Health or local authorities of licences (hereinafter referred to as 'milk licences') authorising the use of that special designation; and

(*c*) prescribe the periods for which, and the conditions (including conditions as to the payment of fees) subject to which, milk licences in general or milk licences of any particular class are to be granted;

(*d*) provide for the revocation or suspension of a milk licence in the event of a breach of any condition subject to which the licence was granted; and

(*e*) provide for entitling any person aggrieved by the refusal, suspension or revocation of a milk licence by a local authority to appeal to the Minister of Health; and

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* **H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 4d. net.**

(*f*) provide for such matters as are necessary for giving effect to, or are incidental to, or consequential on, any provisions contained in the order by virtue of the foregoing provisions of this subsection.

"(2) No person shall, for the purpose of the sale or advertisement of any milk—

(*a*) use a special designation in any manner calculated to suggest that it refers to that milk, unless there is in force a milk licence authorising the use of that designation in connection with that milk; or

(*b*) refer to that milk by any such description, not being a special designation, as is calculated falsely to suggest either that the cows from which the milk is derived are free from the infection of tuberculosis or of any other disease, or that the milk is tested, approved or graded by any competent person.

"(3) In any proceedings taken by virtue of paragraph (*b*) of the last foregoing subsection it shall lie on the defendant to prove the truth of any suggestion which, in the opinion of the court, his acts or conduct as proved by the prosecution are or is calculated to convey."

(2) Section 14 of the Milk and Dairies (Amendment) Act, 1922 (which provides that, in the application of that Act to Scotland, references to the Department of Health for Scotland shall be substituted in the Act for references to the Minister of Health) shall have effect as if at the end of paragraph (*a*) of that section there were inserted the words "and the Department of Agriculture for Scotland shall be substituted for the Minister of Agriculture and Fisheries."

(3) Any order under sec. 3 of the Milk and Dairies (Amendment) Act, 1922, which is in force immediately before the commencement of this Act shall continue in force until revoked.

Statutory Rules and Orders

1934, No. 1317*

MILK AND DAIRIES, ENGLAND

THE MILK (SPECIAL DESIGNATIONS) ORDER, 1934, DATED NOVEMBER 28, 1934, MADE BY THE MINISTER OF HEALTH UNDER SEC. 3 OF THE MILK AND DAIRIES (AMENDMENT) ACT, 1922 (12 & 13 GEO. 5, C. 54).

The Minister of Health after consultation with the Minister of Agriculture and Fisheries in exercise of the powers conferred on him by sec. 3 of the Milk and Dairies (Amendment) Act, 1922, as enacted in sec. 10 of the Milk Act, 1934 (*a*), and of any other powers enabling him in that behalf hereby orders as follows:

1. This Order may be cited as the Milk (Special Designations) Order, 1934, and shall come into operation on the date hereof.

2. In this Order "the Minister" means the Minister of Health.

3. The special designations which may be used in relation to milk under a licence granted by the Minister are "Certified" and "Grade A (Tuberculin Tested)".

4. The Minister may grant licences to producers to use the special designations "Certified" and "Grade A (Tuberculin Tested)" in relation to milk.

5. This Order shall have effect as if the following Articles and Schedules of the Milk (Special Designations) Order, 1923(*b*), were with any necessary modifications incorporated herewith, that is to say, Articles 2, 5, 6, 7, 8, 9(1) and 12 and the First Schedule (Form A), the Second Schedule, the Third Schedule, Part I, Part II, Part IIIA(7) and C(2) and the Fourth Schedule.

6. Any licence heretofore issued by the Minister on or after the fifteenth day of August nineteen hundred and thirty-four authorising the sale of milk as "Certified" or "Grade A (Tuberculin Tested)" shall if the period for which the licence was issued has not expired on the date of this Order be deemed to have been granted under this Order and shall for the remainder of such period have effect as if it were a licence granted under the appropriate provisions of this Order.

(*a*) 24-5 G. 5, c. 51. (*b*) S.R. & O. 1923 (No. 601), p. 564.

* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 1d. net.

Fruit and Vegetable Preservation Research Station, Campden

ANNUAL REPORT, 1933–1934*

IN 1930 the canning industry became more intimately associated with the management of the Station, and, as a result of the financial support received from commercial firms, the scope of the work has increased year by year. The Report reviews the progress that has been made during the last four years. The Station now possesses chemical, biochemical, physical and bacteriological laboratories, and experimental rooms fitted with machinery for canning fruit and vegetables and milk products on a moderately large scale. Experimental and research work on problems in connection with the canning of food products has been continuously carried out, and the results have been published in various bulletins. An account of some of the important lines of research work is given in the present report, with brief notes on results obtained in various investigations.

HYDROGEN SWELLS.—A second bulletin incorporating certain fundamental features is to be published shortly. It deals *inter alia* with the influence of the tinplate, effects produced by the can-making process, by the raw products, and by the canning processes, and chemical studies of corrosion effects in tins.

The chemical composition of the base plate, particularly in respect of the presence of small amounts of other metals, appears to be of extreme importance. This has led to the testing of cans made from a new type of tinplate, known as strip-plate, in which the less desirable elements are present in smaller quantities.

LACQUER TESTS.—Very satisfactory results have recently been obtained with new lacquers, and in the latest experiments lacquer surfaces have remained intact and purple fruits free from discoloration after 5 months' storage at 95° F.

CANE AND BEET SUGAR.—As many canners were decidedly prejudiced against the use of beet sugar, comparative tests with syrups containing beet and cane sugar were made. These showed conclusively that beet was as satisfactory as cane sugar from every point of view, and at present British beet sugar is probably more extensively used than the imported cane sugar.

RIPENING OF PEAS.—An investigation is in progress to ascertain the tendency of each variety of peas to ripen at a fast or slow rate. The ripening of the crop as a whole and the stages of ripening of pods of the same maturity are both being studied.

INFLUENCE OF SOIL ON COLOUR OF VEGETABLES.—Beetroots and carrots have been grown under similar conditions in the Campden area. The colour of the canned products is being determined by means of the tintometer, and an attempt will be made to correlate the results with the chemical and physical properties of the soils.

CHANGES IN HYDROGEN-ION CONCENTRATION IN SYRUPS.—The results obtained in an investigation are summarised in the following table. In each case

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* Published by the University of Bristol. Pp. 85. Introduction by F. Hirst, M.Sc. (*Director*), and contributions by W. B. Adam, M.A., A.I.C., G. Horner, M.Sc., R. Hull, B.Sc., and G. Stanworth.

12 ounces of fruit were packed in A2 cans, the filling temperature being 170° F., the exhaust 6 minutes at 180° F., and the sterilising time the normal period of stationary cooking for each class of fruit.

	End of exhaust	Mid-cook	End of cook	1 hr. cool	1 day's storage	5 days' storage
Gooseberries ..	3·36	3·14	2·93	2·85	2·82	2·82
Strawberries ..	—	3·84	3·63	3·60	3·55	3·55
Raspberries ..	4·25	3·70	3·43	3·34	3·10	3·10
Loganberries ..	3·42	2·90	2·72	2·70	2·70	2·70
Blackcurrants ..	3·86	3·48	3·24	3·18	3·16	3·16
Cherries (sweet) ..	—	5·83	4·33	3·99	3·72	3·70
Pershore plums ..	5·96	3·03	3·00	2·94	2·90	2·87
Victoria plums ..	5·48	3·12	3·08	3·02	2·97	2·95
Damsons ..	3·55	3·05	2·98	2·94	2·93	2·93
Blackberries ..	3·44	2·98	2·86	2·84	2·84	2·83
Bilberries ..	3·56	3·15	3·10	3·02	3·00	3·00

By the end of the full cooking period nearly all the syrups were very close to the constant *p*H value; exceptions were noted for raspberries and cherries, with which the diffusion process was rather slow. The *p*H value appears to be virtually stable in nearly all cases within 1 to 2 days after canning.

Changes in Acidity.—The following table shows the rate of diffusion of acid into syrup of various fruits:

Acidity expressed as per cent. citric acid

	Mid-cook	End of cook	1 hr. cool	1 day's storage	5 days' storage
Gooseberries	0·23	0·49	0·70	1·15	1·15
Strawberries	0·13	0·20	0·29	0·33	0·41
Raspberries	0·08	0·10	0·22	0·60	0·63
Loganberries	0·36	0·52	0·85	1·48	1·62
Blackcurrants ..	0·48	0·66	0·78	0·95	1·30
Cherries (sweet) ..	0·02	0·03	0·03	0·09	0·18
Pershore plums ..	0·20	0·29	0·52	1·01	1·17
Victoria plums ..	0·28	0·33	0·55	0·86	0·90
Damsons	0·35	0·52	0·88	1·48	1·83
Bilberries	0·22	0·28	0·32	0·43	0·57

The rise in acidity of the syrup corresponds very closely with the fall in density, stability being reached most rapidly with most soft berries, and more slowly with stone fruits and currants.

Inversion of Sugars.—After short stationary cooking periods the extent of inversion immediately after canning and cooling ranged from 2 per cent. for cherries to 20 per cent. for blackcurrants. Long stationary cooking periods gave about twice these figures. The percentages increased considerably during the next few days (10 to 15 per cent. for cherries and strawberries to 35 per cent. for blackcurrants). Subsequent conversion of sucrose into invert sugar goes on slowly during storage. A very high percentage of invert to total sugars in a can is usually a sign of excessive heating during processing, or of a high temperature or long period of storage. The following table shows results of tests on the rate of inversion of canned fruits stored at normal temperatures:

Inversion expressed as per cent. of total sugars

	*p*H	4 months' storage	6 months' storage	8 months' storage
Gooseberries	2·72	61·8	67·3	—
Raspberries	3·35	24·5	24·7	26·1
Loganberries	2·88	45·5	49·6	—
Cherries (sweet) ..	4·00	27·9	27·9	28·0
Blackcurrants ..	3·17	39·5	46·1	4·80
Greengages	3·08	32·1	33·8	38·5
Pershore plums ..	2·80	37·0	38·2	46·8
Victoria plums ..	2·88	35·7	38·9	47·2
Damsons	2·93	39·5	53·1	62·6
Blackberries	2·95	36·3	43·0	46·0

TEXTURE OF CANNED FRUITS AND VEGETABLES.—An apparatus for measuring the toughness of fruits and vegetables has been designed, and is described in the report. It has been found that different parts of the skins of fruit are of different toughness. Hard water used in preparing the syrup or brine does not appreciably toughen the skins of fruits or most fresh vegetables, but the toughness of the skins of fruits increases with the strength of the sugar syrup used.

GASES IN CANNED FOODS.—A description is given of an apparatus designed for the collection of the headspace gases from canned fruits and vegetables. The composition of the gases immediately after canning depends largely upon the relation between the size of can, fill and headspace. When the headspace is large, the proportion of entrapped air is high and the percentage of carbon dioxide low. The ratio of oxygen to nitrogen can never have a value as high as that for air (0·264), as the gas from the tissues of the fruit contains only traces of oxygen as against considerable amounts of nitrogen.

The changes that take place in the headspace of canned fruits are due largely to some corrosive process. The oxygen-content usually decreases to zero before any appreciable amount of hydrogen is evolved. When the oxygen has almost disappeared, therefore, the headspace contains only carbon dioxide and nitrogen, and the vacuum is usually perceptibly higher than when the cans were first packed. These changes are illustrated by a series of tables. The results show that the oxygen is removed from the can by about 7 to 10 days' storage in plain cans and 4 to 6 weeks in lacquered cans, whilst, in the earliest stages of hydrogen development, the rate of corrosion, as measured by the gas changes, is greater in plain cans. It is well known, however, that lacquered cans give much greater losses from hydrogen swells than plain cans, and, therefore, at some period of storage the rate of development in lacquered cans must show an increase.

SPOILAGE OF PROCESSED FRUIT BY *Byssochlamys fulva*.—An investigation made with the object of determining the possibility of factory control led to the following conclusions:—A small percentage germination of ascospores took place slowly at 65° C. At 70° to 80° C. the rate of germination and percentage germination were stimulated; above this maximum, heating retarded germination and killed the ascospores. Increase of time of heating at 65° to 70° C. had a stimulating effect, but increase of time of heating at 75° C., 80° C. and 85° C. led to decreased rate of germination and percentage germination.

MEASUREMENT OF VACUUM IN SEALED CANS.—Two methods of measuring the vacuum were investigated, *viz.* the "flip" method and a method based on the depression of the ends of the cans, the standard surface from which the readings were taken being the flat portion of the countersink. It was found that the movements of the ends—up to a vacuum in the region of 15 inches—bore a definite relationship to the vacuum within the can. Above that vacuum the ends become permanently strained inwards. Experiments on the effect of vacuum on the volume of the can are recorded.

U.S.A. Department of Commerce

NATIONAL BUREAU OF STANDARDS

IRON GALLATE INKS—LIQUID AND POWDER*

In view of complaints by the U.S. Post Office Department of excessive corrosion of steel pens caused by the ink used in their stations, a general study of writing inks has been undertaken in an attempt to prepare one that would be less corrosive than the standard ink, and which could also be prepared in the form of a powder and still comply with the requirements of the specification (Federal Specification TT-I-563, Ink; Writing).

The standard writing ink contains 3 g. of iron per l., and this proportion was used in all the experimental work. The characteristics of the inks were tested by the Specification methods, and an attempt was made to evaluate the stability in terms of the number of days required for sediment to appear. Although the results for individual inks were not strictly reproducible, they always placed the inks in the same order of stability.

Since gallic acid inks are known to be more stable than inks made from tannic acid, preparations containing increasing amounts of gallic acid and decreasing amounts of tannic acid were tested, and the following results were obtained:

	Composition of ink in g. per litre						
	Tannic acid	Gallic acid	Ferrous sulphate, $FeSO_4.7H_2O$	Ferric sulphate, anhydrous	Oxalic acid	Tartaric acid	Stability as approx. days for sediment to form
1* ..	11·7	3·8	15	—	—	2·6	5
2 ..	8·4	7·7	15	—	—	2·6	5
3 ..	—	10	15	—	—	2·6	10
4 ..	11·7	3·8	—	10·7	2·16	—	7
5 ..	8·4	7·7	—	10·7	2·16	—	35
6 ..	—	10	—	10·7	2·16	—	42†

* Standard ink is similar to this, excepting that 12·5 g. of U.S.P. hydrochloric acid is substituted for tartaric acid, and 3·5 g. of dye and 1 g. of phenol are added.

† Test stopped before sediment appeared.

Rupert (*Ind. Eng. Chem.*, 1923, **15**, 489; Abst., ANALYST, 1923, **48**, 459) found that inks containing gallic acid without tannic acid were not very permanent when exposed to atmospheric conditions. In the present experiments, however, stripes of the inks were exposed for 150 hours in a Fade-ometer, and the two types of ink were equally permanent.

In comparative experiments with inks respectively containing Walther's patent ferric chlorosulphate hexahydrate (*Chem.-Ztg.*, 1921, **45**, 842), ferric chloride and ferric sulphate, no marked differences were observed in keeping qualities or corrosive action, but ink powder prepared with ferric chlorosulphate began to cake after 2 months' exposure to an atmosphere with 50 per cent. relative humidity, whereas powders containing the other two salts remained loose.

Inks stabilised with tartaric, citric or succinic acid kept as well as the standard ink. In Walther's formulae inks made with ferric chlorosulphate require to be stabilised with oxalic acid. The amount of hydrochloric acid in the Specification standard ink is chemically equivalent to 2·16 g. of crystallised oxalic acid or 2·58 g.

* Research Paper R.P. 807, by E. W. Zimmerman, July, 1935.

of tartaric acid, and these acids are suitable for stabilising ink powders. Oxalic acid is an effective stabilising agent for inks made with ferric salts, because it also retards the corrosion of pens by forming a protective film of ferrous oxalate upon them. The corrosion decreases with increase in the concentration of oxalic acid. On the other hand, oxalic acid has been shown to have a deleterious effect upon the ageing of paper (*J. Research National Bureau of Standards*, **1935**, **14**, **463**; RP 779), and this type of ink is therefore unfit for use in making permanent records.

The following formulae were worked out for ink, in liquid or powder form, from the data obtained in these experiments:

	Ink		
	No. 16 g.	No. 17 g.	No. 18 g.
Gallic acid	10·0	10·0	10·0
Ferric sulphate, anhydrous	10·7	—	—
Ferrous sulphate, $FeSO_4.7H_2O$	—	15·0	15·0
Oxalic acid	2·0	—	—
Tartaric acid	—	1·0	—
Sulphuric acid, as anhydrous H_2SO_4	—	—	0·654
Soluble blue (C.I. 707)	3·5	3·5	3·5
Water to make	1 litre	1 litre	1 litre

Ink No. 16 and 17 can be prepared as powders which, when dissolved in the proper amount of water, will make inks that comply with the Federal Specification requirements. Ink No. 18 cannot be prepared in powder form. To make 1 gallon (U.S.A.)* of ink, the figures given must be multiplied by 3·79. All the inks are more stable and less corrosive to pens than the standard ink. Ink No. 17 is less stable than the other two, and it contains oxalic acid, which attacks paper and tends to form a crust on steel pens.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Ammonium Salts as an Indication of the Quality of Milk. A. I. Burstein and F. S. Frum. (*Z. Unters. Lebensm.*, 1935, **69**, 421–431.)—The methods of Tillmans, Splittberger and Riffart (Abst., ANALYST, 1914, **39**, 173) and of Grünhut (*Z. Unters. Nahr. Genussm.*, 1919, **37**, 304) are tedious and complicated, and the authors have therefore used Folin's rapid method (*Chem.-Ztg.*, 1924, **48**, 557) in this investigation. Three g. of sodium permutit are placed in a 200-ml. graduated flask and washed by decantation first with a little 2 per cent. acetic acid and then two or three times with water. Fifty ml. of milk are added and shaken well with the permutit for several minutes, and, after the permutit has settled out completely, the milk is decanted and replaced by water, the shaking and decantation being repeated with additional quantities of water until the decanted liquid is quite clear. Ten to 20 ml. of water are added to the permutit and 5 ml. of 10 per cent. sodium hydroxide solution, to liberate ammonia from the ammonium permutit, the flask is then nearly filled with water, 5 ml. of Nessler's reagent are added, and the volume is made up to 200 ml. A standard comparison solution is prepared in the same manner, 1 ml. of an ammonium sulphate or ammonium chloride solution corresponding with 0·1 mg. of ammonia being used instead of the milk (3·8792 g. of ammonium sulphate or 3·147 g. ammonium chloride per 1., the working solution being prepared from this by ten-fold dilution). The solution prepared from the milk is compared colorimetrically with the standard solution. The water and acetic acid used must be freed from ammonium salts by treatment with permutit. The determination takes from 30 to 40 minutes, and the authors have established by experiment that no material amount of ammonium compounds remains in the milk.

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* The U.S. gallon = 0·833 imperial gallon.

A series of determinations showed that the concentration of ammonia in quite fresh milk (30 to 40 minutes after milking) is 0·10 to 0·12 mg. per 100 ml., thus contradicting statements in the literature that fresh milk contains no ammonium compounds. The dependence of the concentration of ammonia upon the time and temperature of storage of milk was investigated. Milk stored in the laboratory at 10 to 12° C. gave on the first day an acidity (Thörner scale) of 16·42, and an ammonia-content of 0·184 mg. per 100 ml. On the sixth day the acidity was 39·61, and the ammonia-content 0·575. The intermediate values, when plotted on graph paper, form curves which are approximately parallel. With milk stored at 18 to 20° C. the acidity rose from 21·25 initially to 113·99 on the fourth day, the initial and final concentrations of ammonia being 0·180 and 0·470 mg. per 100 ml. In this instance the acidity curve indicates a sharp rise to the curdling point on the second day, the ammonia curve showing a similar, but relatively smaller rise. The curves are again similar in shape. Milk kept at 2 to 3° C. showed very little change in acidity in 4 days, but the ammonia concentration rose from 0·156 to 0·308 mg. per 100 ml. These results are in accordance with the known temperature limits of the activities of the bacteria causing the souring of milk. At the higher temperatures the lactic acid bacteria are most active, whilst at lower temperatures the proteolytic bacteria develop. As might be expected, the concentration of ammonium salts rises more rapidly in unclean than in clean milk. The addition of sodium carbonate as a preservative (1 mg. per ml.) tends to cause a slight increase in the rate of formation of ammonium compounds. Alteration of the *p*H value towards the basic side favours the development of proteolytic bacteria.

On the basis of these results the authors suggest the division of milk samples into 3 classes: (*a*) Milk of the best quality, 0·10–0·12 mg. of ammonia per 100 ml.; (*b*) milk of medium quality, 0·15–0·18 mg. per 100 ml.; (*c*) milk admissible for immediate use, 0·22–0·23 mg. per 100 ml. A. O. J.

Detection of Coal-tar Colours in Hens' Eggs. J. Grossfeld and H. R. Kanitz. (*Z. Unters. Lebensm.*, 1935, **69**, 582–584; *cf.* ANALYST, 1935, 253.)—An emulsion sold as "Regina red" for adding to poultry food in order to colour the yolks of the eggs obtained, is found to contain a colouring matter of the Soudan class. The dye does not find its way into the egg immediately, but after the material had been employed for some time the dye could be detected in 17 of 20 yolks examined. For testing, the separated yolk is mixed thoroughly with a mixture of 10 ml. of 95 per cent. alcohol and 30 ml. of ether, and the extract is filtered off. About 5 ml. of the filtrate are treated, in a test-tube, with 1 ml. of 5 per cent. sodium nitrite solution and a few drops of hydrochloric acid, and vigorously shaken. The nitrous acid bleaches the natural colouring matters of the yolk and the Soudan dyestuff is shown by its bright red colour, which persists unchanged even after 24 hours.

Another procedure consists in extracting two yolks with the above alcohol-ether mixture, evaporating the solvent from the extract, saponifying the residue with alcoholic potassium hydroxide, adding water, and shaking with petroleum spirit. The natural yellow colouring matters in the petroleum spirit extract are then destroyed by nitrous acid, a pink colour appearing. After the solvent has been evaporated, the residue is taken up in 5 ml. of hot alcohol, and the solution is cooled in ice. Most of the cholesterol is thus separated, and, after removal of this by filtration, the red alcoholic solution is poured into 75 ml. of water acidified with tartaric acid. The cholesterol still present, together with part of the artificial colouring matter, is thrown out, and the remaining solution slowly imparts a pink colour to woollen yarn immersed in it. In alcohol-ether extracts prepared as above from the natural colouring matters, capsanthin, carotene, and bixin, these are almost completely decolorised by nitrous acid. T. H. P.

Decomposition and Preservation of Eggs. A. Tanke and L. Jirak. (*Z. Unters. Lebensm.*, 1935, **69**, 434–452.)—During the storage of eggs two different processes affecting their quality take place, *viz.* loss of water from the white and exchange of material between yolk and white. These result in a decrease in the refractive index of the yolk and an increase in that of the white. Since, in fresh eggs, the yolk has a distinctly higher refractive index than the white, these changes cause a decrease in the difference between the two refractive indices. If n_D^D is the refractive index of the yolk and n_D^K that of the white (both determined with sodium light) the expression $1000\ (n_D^D - n_D^K)$ is termed the "quality number" (*Wertzahl*) of the egg, and is denoted by WZ. The minimum value of the refractive index of the yolk of fresh eggs is 1·420 at 17·5° C. The expression $1000\ (1{\cdot}420 - n_D^D)$ is termed the "age number" (*Älterungzahl*), and is denoted by AZ. Negative values of AZ are recorded as zero. The procedure for the determination of these values is as follows:—The egg, after examination by transmitted light to detect infection, is broken, and the white is separated from the yolk. The white is homogenised by drawing it up several times into a pipette having a fine orifice. A drop is then placed between the prisms of a refractometer (the Abbé type is recommended), and the observation is made at room temperature. A specimen of the yolk, taken by piercing the yolk-sac by means of a finely-drawn-out glass tube, is mixed well and homogenised, and the refractive index is determined. The following minimum values for the refractive index of fresh yolk are given:

Temperature	15° C.	16° C.	17·5° C.	18° C.	20° C.	22° C.	24° C.	26° C.
$(n_D)^D$	1·4204	1·4203	1·4200	1·4199	1·4195	1·4190	1·4185	1·4182

These may be used in the determination of AZ at room temperature.

The value of WZ for fresh eggs should be at least 55 and the value of AZ should not exceed 5. By this method the authors investigated the effects of different methods of storing eggs upon their quality. The decisive factors which determine the degree of freshness of an egg are the amount of internal evaporation, the extent to which exchange of material between yolk and white has taken place, and the degree of contamination by micro-organisms. For the cleansing of the outer surface a sodium hypochlorite solution (10 mg. active chlorine per l.) proved the best, but it is difficult to attain complete sterilisation when contamination has penetrated to the inner shell membrane.

Moist preservation completely prevents evaporation from the interior, but there is slight penetration of the aqueous solution into the interior of the egg, and this may cause rupture of the yolk-sac, impairing of the taste, and, in water-glass preservation, discolouring of the albumen. The complete elimination of these undesirable effects by first impregnating the shell with vaseline or paraffin preparations is apparently not attainable. Bacterial infection causes very little loss with these methods, but the ageing process (represented by the AZ value) is scarcely retarded. Lowering the temperature of the store room certainly retards the ageing process, and thus "cold-storage" eggs have the lowest AZ values. Eggs stored at +1° C. showed by the refractometric method values just as good as those stored at about 14° C. for only 40 days. It is suggested that the main disadvantage of cold storage, *viz.* absorption of odour from the filling material in the boxes, could be removed by substituting steel springs for the packing material. A diminution of the internal evaporation by closing the pores in the shell can be effected in various ways. For large-scale operations liquid paraffin alone, or as a solvent for other preparations, is most suitable when mechanical appliances are used to rotate the eggs during spraying. Aqueous preparations, such as thin emulsions, do not spread evenly, and are of use in spraying processes only if the egg is previously coated with a film of such preparations as Tylose or Colloresin. These methods reduce internal evaporation and bacterial infection, but have no marked effect upon the AZ value, unless cold storage is simultaneously adopted. Paste-forming emulsions applied by smearing give good results; losses due to evaporation and infection are diminished, changes due to age are markedly retarded, and no foreign matter is introduced into the interior of the egg. This method has the additional advantage of requiring no special apparatus. A. O. J.

Detection of Rye and Wheat Flour in Mixtures by the Trifructosan-content. H. Werner and H. Volger. (*Z. Unters. Lebensm.*, 1935, **69**, 555–562.) —The method described by Strohecker (*ibid.*, 1932, **63**, 514) for determining rye meal in flour or baked wares depends on determination of the trifructosan found in rye by Tillmans and his co-workers. The modified form of this method used by the present authors is as follows:—Ten g. of the flour are mixed to a uniform paste with 100 ml. of water and then treated with 5 ml. of dialysed colloidal ferric hydroxide solution (to precipitate the proteins), and filtered after 10 minutes through a pleated filter into a 100-ml. measuring cylinder. Of the filtrate, 25 ml. are made up to 90 ml. with 96 per cent. alcohol and, after 10 minutes, filtered into a 50-ml. cylinder. To 45 ml. of the filtrate are added 5 ml. of alcoholic 0·5 *N* potassium hydroxide, the mixture being left for 30 minutes, and then filtered through an Allihn tube and the precipitate washed with two 5-ml. quantities of 96 per cent. alcohol. The precipitate is next dissolved in 20 ml. of hot water, and the solution is collected in a test-tube, inverted by heating with 1 ml. of hydrochloric acid (sp.gr. 1·19), neutralised, and washed with a little water into a beaker. The solution is then boiled for 2 minutes with an equal volume of Fehling solution and the cuprous oxide collected and weighed as cupric oxide in the usual way. If a is the weight of CuO, and w the percentage of dry matter in the flour, the amount of cupric oxide corresponding with 1 g. of dry substance is given by $100a/1{\cdot}19w$.

For a number (17) of wheaten flours the values thus obtained varied from 25 to 33 mg., and for 19 commercial flours from 19 to 35 mg., the mean being 27 mg. Of 18 rye meals, purchased retail, one gave the figure 59 and the rest values ranging from 75 to 111; 32 per cent. lay between 91 and 100 and 23 per cent. between 101 and 110. From the trifructosan-content, it is, therefore, not possible to determine the proportions of rye and wheat meal in a mixed flour. Loss of trifructosan occurs during baking, and the method is inapplicable to bread, etc.

T. H. P.

Occurrence of Acetaldehyde in Tropical Fruits. A. Steinmann. (*Z. Unters. Lebensm.*, 1935, **69**, 479–481.)—In applying Griebel's method (Abst., ANALYST, 1924, **49**, 486) the period of cooling should be extended to 45 minutes before the crystallisation test can be regarded as negative. In most instances Griebel's observation, that acetaldehyde generally occurs in fruits which have a sharp, sour taste when unripe, the sourness disappearing as the fruit ripens, has been confirmed. Negative results were obtained with fruits of the N.O. *Palmae* and *Zingiberaceae*, in which there is no transition from sour to sweet taste, also with *Dialium indicum* (*Leguminoseae*), which retains a sour taste when ripe, with the *Leguminoseae* in general and with the *Cucurbitaceae*. It is remarkable that all the representatives of the *Solanaceae* investigated gave either a negative or only a faintly positive reaction. Certain fruits, *Lansium domesticum* (*Meliaceae*), *Spondias dulcis* (*Anacardiaceae*), *Persea gratissima* (*Lauraceae*), and some others gave a negative result in the unripe state and a positive reaction when ripe. Here, probably, acetaldehyde does not occur until the fruit is ripe. With other fruits: *Areca catechu* (*Palmae*), *Nicolaia* (*Zingiberaceae*), *Artocarpus communis* (*Moraceae*), in the cocoa bean, and in the husk of *Garcinia mangostana* (*Guttiferae*), it was observed that, instead of crystals, yellow droplets were formed, which on standing for a long time gave place to thick yellow crystals of the hydrazone. Probably in these instances other volatile substances which hinder the formation of crystals occur in the reaction mixture. A. O. J.

Determination of Acetaldehyde in Wines and Spirits. P. Jaulmes and P. Espezel. (*Ann. Falsif.*, 1935, **28**, 325–335.)—The influence of varying conditions on the various stages involved in the determination of acetaldehyde in wine and spirit by the bisulphite and iodine method has been studied. The method evolved from the results obtained is a direct iodimetric method, and comprises three stages: combination in a neutral medium of the aldehyde with sodium bisulphite (in excess), oxidation in an acid medium (*p*H below 2) of the excess of sulphite by iodine solution (either standard or not), and titration with standard iodine in an alkaline medium (*p*H 9·5) of the sodium sulphite formed by the dissociation of the aldehyde-sulphite compound. The reagents required are: (1) 0·1 *N* iodine solution; 1 ml. ≡ 2·2 mg. of acetaldehyde; (2) dry neutral sodium sulphite 18·9 g., *N* sulphuric acid 150 ml., water to 1000 ml.; (3) KH_2PO_4 3·35 g., $Na_2HPO_4.12H_2O$ 15 g., water to 1000 ml., or $Na_2HPO_4.12H_2O$ 24 g., *N* H_2SO_4 25 ml., water to 1000 ml.; (4) hydrochloric acid of 22° Baumé [sp.gr. 1·18] 250 ml., water to 1000 ml.; (5) boric acid 17·5 g., *N* sodium hydroxide 800 ml., water to 2000 ml.; (6) freshly made 0·2 per cent. starch paste.

Fifty ml. of solution (3), 10 ml. of (2) and a definite volume of the aldehyde solution containing 0·01 to 0·03 g. of acetaldehyde are placed in a 250-ml. Erlenmeyer flask, which is stoppered, well shaken, and left for 20 minutes. One ml. of starch paste, 100 ml. of water, and 10 ml. of reagent (4) are added, and solution (1) is run in from a burette until a blue colour just appears. On addition of 1 drop of phenolphthalein solution and 100 ml. of solution (5), the blue colour disappears and the liquid turns pink. The liquid is then titrated with 0·1 *N* iodine solution (*n* ml.) to a blue-violet colour; acetaldehyde taken = 2·2 *n* mg. With wines, the aldehyde should be separated before applying the above method. Two hundred, or 100, or 50 ml. of the wine, according to the acetaldehyde-content, are mixed with 5 per cent. of phosphoric acid and distilled down to the half volume, the distillate being collected in the bisulphite solution and buffer mixture indicated above. Spirits are either treated directly or distilled to concentrate the aldehyde, if this is low in amount. T. H. P.

Occurrence of Sorbitol in Pure Grape Wines. E. Vogt. (*Z. Unters. Lebensm.*, 1935, **69**, 587–591.)—Forty-four wines, mostly of good vintage years, were examined by Litterscheid's method (ANALYST, 1932, **57**, 178), and in only 5 of them—Rülander wines of 1928, 1929, and 1931—was sorbitol found in appreciable quantity. From 600 ml. of the wine, from 30 to 86 mg. of chlorobenzylidenesorbitol, or from 12 to 30 mg. of hexacetylsorbitol were obtained. These amounts are too small to be mistaken as evidence of adulteration with fruit wines, even if such adulteration were likely with these high-grade wines. The value of the sorbitol test is thus confirmed. T. H. P.

Determination of Hydroxymethylfurfural and of Laevulosin in Port Wines and other Sweet Wines. C. I. Kruisheer, N. J. M. Vorstman and L. C. E. Kniphorst. (*Z. Unters. Lebensm.*, 1935, **69**, 570–582.)—To determine hydroxymethylfurfural, 50 ml. of the wine are neutralised to litmus paper by addition of *N* sodium hydroxide and extracted for two days with ether in a percolator. To the percolate (about 50 ml.) are added 10 g. of anhydrous sodium sulphate and, with swirling, 25 ml. of petroleum spirit (b.p. 40 to 60° C.). The next day the dried liquid is filtered into a 200-ml. Erlenmeyer flask, and the precipitate is washed several times with a 1 : 1 mixture of the petroleum spirit and ether. The total filtrate is distilled on a water-bath, the last traces of liquid being expelled by immersing the flask as far as possible in the boiling water and passing through the flask for 10 minutes a current of dry, oxygen-free carbon dioxide. The flask is quickly cooled and, after addition of 10 ml. of 16 per cent. hydrochloric acid, whisked round for a short time, the liquid being then filtered through a small filter-paper, which is washed with about 10 ml. of the acid in small amounts. A fresh, filtered solution of 0·25 g. of phloroglucinol in 30 ml. of hydrochloric acid (16 per cent.) is next added, to give a total volume of 50 ml. The presence of hydroxymethylfurfural is shown by a red colour, changing to an opalescence, and later to a red precipitate; otherwise no precipitate appears even after 24 hours. On the following day the precipitate is collected in a crucible with a porous porcelain bottom (Schott 1G4), if necessary with gentle suction, and is washed with a total of 15 ml. of about *N* hydrochloric acid, dried at 100° C. and weighed. Two, 4, 6, . . . 36 mg. of the phloroglucide correspond respectively with 2·3, 3·3, 4·3, . . . 16·3 mg. of hydroxymethylfurfural, the relationship being linear between 6 and 36 mg. of the phloroglucide.

A useful orienting test may be made beforehand by treating 2 ml. of the wine (if dark, this should be first decolorised with a little norit) in a test-tube with 2 ml. of hydrochloric acid (30 per cent.) and 1 ml. of a fresh 0·5 per cent. solution of phloroglucinol in hydrochloric acid (16 per cent.). If an opalescence appears within 15 minutes or, with a decolorised wine, within 1 hour, the presence of hydroxymethylfurfural is probable. When hydroxymethylfurfural is added to a wine, the above method indicates, not the whole, but the bulk of the addition (240 mg. added; 214 mg. or, in presence of much sulphite, 198 mg. found). Pure ports, free from caramel or added boiled-down must, contain little or no hydroxymethylfurfural, 50 mg. per litre being exceptional. Neither pasteurisation nor long storage affects the content.

Pure ports contain no laevulosin, but in certain sweet wines made with the help of boiled must, this compound occurs in conjunction with hydroxymethylfurfural. To determine laevulosin, 50 ml. of the wine, mixed with 150 ml. of water, are fermented with 10 g. of pure pressed yeast for 2 days at about 30° C., and then neutralised to neutral red by means of baryta solution, centrifuged, and evaporated to about 100 ml. on a water-bath. The subsequent procedure is that previously described (ANALYST, 1933, **58**, 231). T. H. P.

Differentiation of Spirit Vinegar and Artificial Vinegar. A. Schmidt. (*Z. Unters. Lebensm.*, 1935, **69**, 472–478.)—The procedure followed is that of Wüstenfeld (*Lehrbuch der Essigfabrikation*, 1930, Verlag P. Parey, Berlin). The "oxidation value" is the number of ml. of 0·1 *N* potassium permanganate solution required to impart a permanent red colour to 50 ml. of vinegar containing 3 per cent. of acetic acid, in the presence of dilute sulphuric acid. Artificial vinegar prepared from "vinegar essence"* requires not more than 1 or 1·5 ml., whilst spirit vinegar requires 8 ml. or more. As vinegar containing caramel as colouring matter gives very high values (12 to 14 ml.), the oxidation value was determined both before and after treatment with active carbon for 2 minutes at room temperature. Pure glacial acetic acid diluted to 3 per cent. with distilled water gave an oxidation value of 0·2 before treatment with active carbon, and 0·19 after treatment. Fourteen samples of commercial "vinegar essence," containing 3 to 3·5 per cent. of acetic acid and coloured with synthetic dyes, gave oxidation values of 0·9 before treatment with active carbon, and 0·78 after treatment. Sixty samples of commercial vinegar, labelled "fermentation vinegar," containing 2·6 to 3·5 per cent. of acetic acid and coloured with synthetic dyes, gave oxidation values of 5·0 to 7·0 before treatment with active carbon, and 3·2 to 4·1 after treatment.

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* "Vinegar Essence" is the commercial name of a product containing 12 per cent. of acetic acid (made by the distillation of wood or by a synthetic process) and coloured with caramel or an aniline dye. Some years ago "Essigsprit" (a 12 per cent. spirit vinegar) was also sold as "vinegar essence." "Spirit acid" was the concentrated acetic acid obtained by the distillation of *Essigsprit*.—EDITOR.

The iodine value is also determined, as described by Wüstenfeld (*loc. cit.*). Excess of 0·01 *N* iodine solution is added to 25 ml. of vinegar which has been made alkaline, the mixture is allowed to stand for 15 minutes and acidified with dilute hydrochloric acid, and the iodine is titrated back with 0·01 *N* sodium thiosulphate solution. The determination is made both before and after treatment with active carbon for 2 minutes at room temperature, and samples of vinegar containing more than 3 per cent. of acetic acid are diluted to that concentration. Spirit vinegar gives an iodine value of 30 to 60 or more. If the value falls below 20, the sample may be regarded with suspicion. Fifteen samples of artificial vinegar prepared by dilution of glacial acetic acid gave iodine numbers of 5 to 7 before treatment with active carbon and 4 to 6 after treatment. Twenty-four samples of 3 per cent. vinegar prepared by dilution of a 12 per cent. commercial "vinegar essence" gave iodine values of 3 to 5 before treatment with active carbon, and 3 to 4·5 after treatment. Forty-eight samples of commercial fermentation vinegar gave iodine values of 38 to 44 before treatment with active carbon, and 34 to 40 after treatment. The oxidation and iodine values thus afford means of distinguishing between spirit vinegar and artificial vinegar, especially when interpreted in conjunction with other analytical data. (*Cf.* ANALYST, 1927, **52**, 93, 260; 1932, **57**, 722; 1933, **58**, 619.) A. O. J.

Itoyo Fish Oil. S. Ueno and S. Komori. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 345–352B.)—Itoyo oil is obtained from the Gasterostenus family, and the sample of oil used in this investigation was obtained from *G. aculeatus* (Limeoseus). The oil was an orange-red liquid, of sp.gr. 20/4° C., 0·9232, n_D^{20} 1·4789, saponification value 186·9, iodine value (Wijs) 165·0, acid value 0·75, and unsaponifiable matter 1·01 per cent. The mixed fatty acids (free from unsaponifiable matter) had iodine value 171·9, and neutralisation value 190·5. The solid (14·3 per cent.) and liquid (85·7 per cent.) acids were separated by the lead salt and alcohol method. The methyl esters of the fatty acids were prepared and fractionally distilled, and the fractions were analysed. The approximate composition of the oil is regarded as: total saturated acids, about 18·2 per cent., consisting of myristic, 3·7; palmitic, 12·8; stearic, 1·7; and a minute quantity of C_{20} (?) acid. The unsaturated acids contained an acid $C_{16}H_{30}O_2$ (probably zoomaric acid), oleic and catoleic acids, and highly unsaturated acids, $C_{18}H_{28}O_2$ (probably moroctic acid), and $C_{22}H_{34}O_2$ (probably clupanodonic acid). The sterol portion of the unsaponifiable matter was cholesterol, and the liquid portion contained oleyl alcohol, together with a new higher and highly unsaturated alcohol. D. G. H.

New Reaction of *Helvella esculenta*. G. Reif. (*Z. Unters. Lebensm.*, 1935, **69**, 585–586.)—A number of fungi have been tested with the solution of selenious acid in sulphuric acid suggested by Mecke (*Z. öffentl. Chem.*, 1899, **5**, 351) as a sensitive reagent for opium alkaloids and shown later by Levine (*J. Lab. Clin. Med.*, 1925–1926, **11**, 809) to react also with various phenols. Of the fungi examined, only *Helvella esculenta* showed any reaction with the reagent, giving first a red colloidal solution of selenium and later a red precipitate of amorphous selenium. Failure to react was displayed by *Amanita phalloides*, *A. mappa*, *A. muscaria*, *A. pantherina*, *A. rubescens*, *Psalliota campestris*, *Boletus edulis*, *Tricholoma equestre*, *Russula vesca*, *R. emetica*, and various *Morchella* species, including the edible morel (*M. esculenta*), *M. conica*, and *M. semilibera*. The reaction thus provides a means of distinguishing between *Helvella esculenta* and *Morchella* species. The reacting substance remains in the residual solid when the fungus is pressed, but is completely removed by extraction with hot water. It occurs in both the stem and the cap of the fungus and is not destroyed by drying the fungus. In applying the test, 2(0·2) g. of the finely-sliced fresh (dried) fungus are heated with 15 ml. of water on a water-bath for 15 minutes, the cold filtered extract being treated with 15 drops of a solution of 0·5 g. of selenious acid in 100 g. of concentrated sulphuric acid and heated similarly. T. H. P.

Determination of Oxydimorphine. B. Drevon. (*J. Pharm. Chim.*, 1935, **127**, 97–106.)—Oxydimorphine or its salt is dissolved in 1 to 2 ml. of sulphuric acid (sp.gr. 1·83), and on to the surface 0·1 to 0·2 ml. of acetic anhydride is pipetted, the tube being kept cool. A bright green colour appears at the line of separation and gradually spreads through the solution, attaining its maximum intensity in 30 minutes at ordinary temperature. The colour disappears on addition of water, re-appearing with further additions of sulphuric acid. Morphine itself gives no colour under the same conditions. For purposes of comparison the alkaloid must always be dissolved in the same volume of reagent (20 ml. of sulphuric acid and 1 ml. of pure acetic anhydride are mixed without allowing the temperature to rise and used immediately). The green colour developed in this reaction may be compared with stable standards prepared from a mixture of 1 ml. of copper nitrate solution (15 per cent.), 1 ml. of nickel nitrate solution (20 per cent.), and 0·3 ml. cobalt nitrate solution (10 per cent.). The colorimetric determination of oxydimorphine necessitates the isolation of the substance in an insoluble form, and the subsequent application of the above method. To 5 ml. of the solution under examination are added 5 drops of a 5 per cent. solution of silicotungstic acid and about 0·03 g. of potassium bicarbonate. The tube is placed in ice for about 30 minutes, and one drop of a suspension of gelatinous barium sulphate containing about 10 per cent. of the dry product is added. The whole is mixed and centrifuged for three minutes (3000 revolutions), another drop of the suspension is added and centrifuging is repeated so that the alkaloidal precipitate is covered with a layer of barium sulphate. The clear supernatant liquid is withdrawn, and the tube is dried by means of filter paper. After the tube has been cooled in ice, 2 ml. of the acetosulphuric reagent are added, and, after a few minutes' cooling, the mass is brought into suspension by means of a glass rod, when the barium sulphate and oxydimorphine dissolve. The tube is allowed to attain laboratory temperature, and after 30 minutes the colour developed is compared with the standards. Optimum conditions are obtained when 5 ml. of the solution to be examined contain 0·4 to 0·1 mg. of oxydimorphine. The error is of the order ±5 per cent. D. G. H.

Gravimetric and Volumetric Determination of Quinidine. R. Monnet. (*J. Pharm. Chim.*, 1935, **127**, 112–119.)—An excess of potassium thiocyanate is added to an aqueous solution of a basic salt of quinidine, and the resulting precipitate is separated and weighed. One g. of the salt weighed corresponds with 0·8468 g. of quinidine. The quinidine solution (containing not more than 0·29 g. of quinidine) is concentrated to about 20 ml., and if acid to litmus, is neutralised with 0·01 *N* sodium hydroxide solution. After addition of 3 g. of potassium thiocyanate and mixing, the solution is again neutralised, if necessary. After 2 hours the liquid is filtered, the precipitate is washed twice with water and 8 times (2 ml. each time) with a saturated solution of quinidine thiocyanate hydrate, dried and weighed. In the presence of quinine, cinchonidine and cinchonine, the determination is carried out in the same way, but after the precipitate has been washed with the saturated quinidine thiocyanate hydrate solution it is washed six times (1 ml. each time) with 96 per cent. alcohol saturated with quinidine thiocyanate hydrate. If present in large quantities, quinine and cinchonidine may be precipitated as basic tartrates. Emetine, papaverine, strychnine, veratrine and berberine are precipitated by thiocyanate in the neutral medium, but aconitine, atropine, brucine, caffeine, cocaine, codeine, coniciene, eserine, hydrastine, hyoscyamine, morphine, pelletierine, pilocarpine, sparteine, thebaine, theobromine, and yohimbine are not precipitated by thiocyanate. No precipitates are given by digitalin, strophanthin, convallamarin, salicin, acetanilide, adrenaline, antipyrine, cryogenine, exalgine, novocaine, phenacetin, pyramidone, stovaine, urea, urethane, and veronal.

For the volumetric determination of quinidine, the solution, containing the quinidine as nitrate or basic sulphate, is concentrated to about 20 ml., and should then contain not more than 0·15 g. Twenty ml. of a 0·1 *N* solution of potassium thiocyanate are added, the solution neutralised if necessary, made up to 50 ml., and filtered after shaking 4 or 5 times during a 20 minutes' period. The first portion of filtrate is neglected, and 25 ml. are used for titrating the excess of thiocyanate by the Charpentier–Volhard method after addition of 10 ml. of 0·1 *N* silver nitrate solution. Then, if n is the number of ml. of 0·1 *N* potassium thiocyanate added, $32{\cdot}4 \times 2 \times n$ is the quantity of quinidine in the sample. This method cannot be applied in the presence of other cinchona alkaloids or of other substances precipitated by potassium thiocyanate in neutral solution. If salts precipitated by silver nitrate in nitric acid medium are present, the alkaloid must be extracted and dissolved in sulphuric or nitric acid. A sufficient excess of salt is not present for the precipitation of the whole of the quinidine, and a correction may be made by adding 6·5 mg. to the weight of quinidine found. The method is simpler and quicker than the gravimetric procedure. D. G. H.

New Specific Reaction for Yohimbine. Pesez. (*J. Pharm. Chim.*, 1935, **22**, 164–165.)—The method, which is analogous to the Pettenkofer reaction, is based on the condensation of yohimbine with chloral in the presence of sulphuric acid. To a mixture of 3 ml. of concentrated sulphuric acid and 0·2 ml. of a 20 per cent. aqueous solution of chloral, is added 0·5 ml. of a solution of a salt of yohimbine, a drop at a time, with continuous agitation. The solution is then warmed at 50° to 60° C., when the rose colour changes to a greenish-blue shade, which gradually turns to a very stable and more pronounced blue. With preparations containing yohimbine it is necessary first to isolate the alkaloid, on account of the interfering effect of any sugars present. A solution in 5 ml. of hot water is therefore extracted with 1 ml. of ammonia and 2 ml. of chloroform, the chloroform layer being washed with water and the test applied to the residue after evaporation. Dilution with 3 ml. of water is without effect, but addition of 10 ml. causes the colour to disappear. The reaction is sensitive to 0·02 mg. of yohimbine hydrochloride, and is specific for this alkaloid; others usually give a yellow to brown colour, or in the case of those which condense with aldehyde compounds (*e.g.* morphine, veratrine or picrotoxine), a red shade. When other aldehydes are used as condensing agents, yellow to brown shades are also usually obtained, although vanillin and salicylaldehyde give a carmine red; these reactions are not specific for yohimbine. J. G.

Test for Citric Acid and a Reagent for the Opium Alkaloids and Phenols. Pesez. (*J. Pharm. Chim.*, 1935, **22**, 160–163.)—The reaction is based on the conversion of citric acid into glyoxal by the formation, first of pentabromoacetone and then, by hydrolysis, of the compound CHO.CO.COOH, which is decomposed into glyoxal (*cf.* Denigès, *Bull. Soc. Chim.*, 1902, **27**; Polonovski, ANALYST, 1921, **46**, 464). In a test-tube are placed 0·1 ml. of the test solution, 0·05 ml. of saturated bromine water, 3 drops of concentrated sulphuric acid and 0·05 ml. of a saturated solution of potassium permanganate, and the mixture is boiled gently. The colour should disappear, but, if the concentration of citric acid exceeds 2 per cent., a precipitate is formed, and in that case 2 ml. or more of sulphuric acid should be added and the heating continued until complete solution is obtained. The liquid is cooled and 0·1 ml. of a 0·05 per cent. solution of codeine is added, and, if no rose colour appears after a few seconds, the solution is warmed on the water-bath, when a blue to violet colour develops. Codeine may be replaced by other reagents, the respective colours in the cold and on the water-bath being as follows:—Resorcinol, rose, wine-red with a pale green fluorescence; thymol, no reaction, blood-red; β-naphthol, very pale green, deeper emerald-green; salicylic acid, no reaction, red to violet; methyl salicylate, rose to violet, greater in intensity. The reaction is almost quantitative, and is sensitive to 0·0002 g. of citric acid, the most sensitive reagent in this case being the warm methyl salicylate; when the amount of citric acid is so small, however, any colour remaining in the solution when it is warmed with the potassium permanganate must be removed by adding a drop of a saturated solution of oxalic acid. The reaction is specific for citric acid, whilst lactic, acetic, tartaric, oxalic, benzoic, salicylic and uric acids produce only a yellow colour in the cold, which turns brown on the water-bath, and is due to liberation of bromine. The reaction may also be used to prepare a solution of glyoxal for use as a test for the phenols mentioned above, or to replace the Denigès methyl glyoxal reagent for the opium alkaloids, the colours obtained being identical in both cases. A mixture of 10 ml. of 10 per cent. citric acid solution, 30 ml. of bromine water, 1 ml. of sulphuric acid, and 10 ml. of a 4 per cent. solution of potassium permanganate is warmed until the colour disappears, 5 ml. of concentrated sulphuric acid being then added and the mixture boiled for a few seconds. J. G.

Separation and Detection of Cocaine in Mixtures of Cocaine and Procaine. C. H. Riley. (*Amer. J. Pharm.*, 1935, **107**, 271–279.)—Small amounts of cocaine hydrochloride may be identified, after separation from large amounts of procaine hydrochloride, by dissolving 200–250 mg. of the sample in 15 ml. of water, and placing the solution in a separating funnel. To this, 0·5 ml. of 0·5 *M* sodium phosphate (Na_2HPO_4) solution and 15 ml. of chloroform are added, and the whole is well shaken. In a second funnel, 15 ml. of a solution, made by mixing 50 ml. of 0·5 *M* citric acid solution and 90 ml. of 0·5 *M* sodium phosphate solution, are placed. A third funnel containing 10 ml. of this solution, and a fourth containing 5 ml. of water, are also required. A plug of cotton-wool is placed in the stems of funnels No. 3 and No. 4. The chloroform in funnel No. 1 is drawn off into funnel No. 2, shaken, and allowed to separate. It is then drawn off into funnel No. 3, and the process repeated. The chloroform is finally shaken with the water in funnel No. 4, and is then run into an evaporating dish. The whole process is repeated, but with 10 ml. of chloroform. To funnel No. 3, 1 to 2 ml. of chloroform are added, and this is then passed into funnel No. 4, and thence to the evaporating dish. The mixed chloroform solutions are evaporated to dryness. If the residue is large (over 10 mg.), a portion is dissolved in 2 *N* hydrochloric acid on a microscope slide, platinic chloride solution is added, and the crystals are examined under a microscope. If the residue is small, it is dissolved in the dish in two drops of the acid, and this is decanted on to the slide and again examined. All the separator stopcocks must be free from grease. If cocaine is suspected in the form of the free base, the sample is dissolved in 15 ml. of chloroform and separator No. 1 is omitted. A more rapid, but less efficient, method is to dissolve the sample in 5 ml. of water, and to pour the solution into a separating funnel of 100 to 200 ml. capacity. To this are added 5 ml. of 0·5 *M* citric acid solution and 5 ml. of 0·5 *M* sodium phosphate solution. The solutions are thoroughly mixed, 10 ml. of chloroform are added, and the whole is well shaken. A plug of cotton-wool is inserted into the stem of the separating funnel, and the chloroform layer is then drawn off into a second funnel containing 5 ml. of distilled water. The contents of the second funnel are shaken, and the chloroform is again drawn off through a plug of cotton-wool into a small evaporating dish. The initial solution is extracted with 5 ml. of chloroform, which is run off into the second funnel as before. After shaking, the chloroform is drawn off into the evaporating dish. The combined chloroform extracts are evaporated to dryness on the water-bath, the dish is cooled, and the residue is treated with two drops of 2 *N* hydrochloric acid solution. This solution is placed on a microscope slide, one drop of 8 per cent. platinic chloride solution is added, and the slide is examined under the microscope for characteristic cocaine crystals. For the determination of the amount of cocaine present, 200 to 250 mg. of the sample are dissolved in 12 ml. of water in a separating funnel. To the solution are added 3 ml. of 0·5 *M* sodium phosphate solution. In a second funnel are placed 15 ml. of a mixture of 10 ml. of 0·5 *M* citric acid solution and 20 ml. of 0·5 *M* sodium phosphate solution; in a third funnel 10 ml. of this solution, and in a fourth 5 ml. of water. Extractions are made with 15 + 10 + 10 ml. of chloroform as before. The chloroform extracts are evaporated to dryness, and the residue is dried and weighed. The residue is then dissolved in neutral alcohol, 20 ml. of 0·5 *N* sulphuric acid solution added, and the excess is titrated with 0·02 *N* sodium hydroxide solution, methyl red being used as indicator. Each ml. of 0·5 *N* sulphuric acid absorbed by the residue is equivalent to 0·015158 g. of cocaine or 0·01698 g. of cocaine hydrochloride. S. G. S.

Quantitative Determination of Diaminoacridine in Euflavine. F. Reimers. (*Quart. J. Pharm.*, 1935, 8, 218–230.)—Inaccuracies in the methods of Gaillot (*Quart. J. Pharm.*, 1934, 7, 63) and Hall and Powell (*Quart. J. Pharm.*, 1933, 6, 389; 1934, 7, 522; Abst., ANALYST, 1935, 108) are pointed out. The difference between the basic strengths of the components of diaminoacridine hydrochloride, as determined from measurements with the glass electrode, may be utilised as the basis of a rapid method which can be employed as a check on the accuracy of other methods. The amount of diaminoacridine hydrochloride in euflavine may be determined more accurately than by previous methods, by dissolving 0·5 g. to 0·7 g. of the euflavine in 10 ml. of boiling water in a 250-ml. flask. To this are added 90 ml. of isopropyl alcohol and 2 ml. of thymol blue solution, and the mixture is titrated with 0·1 *N* sodium hydroxide solution to a definite colour-change, *i.e.* to a colour that is murky brown. The titration must be made in strong electric light. The solution is then titrated back with 0·1 *N* hydrochloric acid solution until the colour no longer changes. As a rule, 0·2 to 0·5 ml. are required for this. The difference between these titrations, multiplied by 0·02462, gives the amount of diaminoacridine hydrochloride in the sample taken. S. G. S.

Biochemical

Presence of Manganese in Cane Sugar and Maple Sugar. P. Riou and J. Delorme. (*Compt. rend.*, 1935, 200, 1132–1133.)—Crude cane sugar and maple sugar both contain manganese, the amount varying in the former up to 4 parts per million, and in the latter from 10 to 125 parts per million. Refined cane sugar contained no manganese, and therefore the small amounts present in the crude sugar are removed during the refining processes. The plant tissues of both the sugar cane and the sugar maple contain manganese, and the authors are extending their work with a view to ascertain if this element has any catalytic effect on the formation of sugar in the plant cells. S. G. S.

Study of the Concentration and Properties of Two Amylases of Barley Malt. M. L. Caldwell and S. E. Doebbeling. (*J. Biol. Chem.*, 1935, **110**, 739–747.)—If extracts of barley malt are subjected to repeated fractionations by ammonium sulphate with intervening dialyses, followed by fractional precipitation with alcohol, it is possible to obtain two distinct amylases. The amylases so prepared are free from carbohydrates, but both give positive protein colour reactions, and both are rapidly inactivated by heat in aqueous solutions. In the presence of 0·01 *M* acetate, and at 40° C. *p*H values of 4·3 to 4·6 favour the saccharogenic action of both types of enzyme. The amylase having a preponderance of an amyloclastic activity also has an optimum *p*H of 4·3 to 4·7. S. G. S.

Measurement of Phenolase Activity. R. Samisch. (*J. Biol. Chem.*, 1935, **110**, 643–654.)—During the study of some of the variables involved in the oxidation of phenols by gaseous oxygen in the presence of plant phenolase, it was found that the rate of enzymic oxidation could be increased if the partial pressure of oxygen was increased to between 60 and 70 per cent. O_2. The oxygen absorption was increased by increasing the concentration of the substrate, but this had an optimum value, beyond which a further concentration of the substrate inhibited enzyme activity. The optimum *p*H value for the activity of the enzyme was found to vary with the source of the enzyme, and also with the nature of the substrate. At moderate temperatures, phenolase activity is destroyed by a reaction which appears to be chemical in nature, and not a heat coagulation. The activity is also inhibited by the halides of neutral salts, the effects of these being in the inverse ratio of their atomic numbers. A phenolase unit is proposed, and is defined as the velocity constant K (= O_2 absorbed/log t) measured in an atmosphere of pure oxygen, at 25° C., at the optimum *p*H value, and with the optimum concentration of the substrate. S. G. S.

Enzymic Method for the Estimation of True Vitamin *C*. H. Tauber and I. S. Kleiner. (*J. Biol. Chem.*, 1935, **110**, 559–563.)—The substances interfering with the chemical determination of vitamin *C* may be eliminated, now that a specific ascorbic acid oxidase has been isolated (ANALYST, 1935, 625). The enzyme is prepared from the pericarp of the Hubbard squash by extracting 250 g. with 750 ml. of 30 per cent. alcohol, and filtering. 0·5 mg. of ascorbic acid should be completely oxidised by 10 ml. of this extract in 30 minutes at 38° C. If the enzyme solution is weaker, incubation time must be increased accordingly. Samples for analysis are prepared by the Emmerie and van Eekelen mercuric acetate method. A standard solution of ascorbic acid is prepared by dissolving 25 mg. of pure ascorbic acid and 50 mg. of cystine in 90 ml. of boiling 0·01 *N* hydrochloric acid solution, cooling and diluting to 100 ml. This solution keeps only for one day. The fluid to be analysed is adjusted to *p*H 5·0 and titrated with 2, 6-dichlorophenone indophenol. This is prepared by extracting 50 mg. of the dye with 150 ml. of boiling water, and is standardised against the standard ascorbic acid solution. It will keep for four days. Another portion of the fluid under examination is treated with 1 ml. of *M* acetate buffer solution of *p*H 6·0 and 10 ml. of the enzyme solution. It is kept at 38° C. for 30 to 60 minutes. The enzyme activity is then stopped by the addition of 1 ml. of 2 per

cent. sulphuric acid solution, and the residual reduction is determined by titration with the dye. The difference between these two titrations is calculated as ascorbic acid.
S. G. S.

Biological Utilisation of Esters of Vitamin *E*. H. S. Olcott. (*J. Biol. Chem.*, 1935, **110**, 695–701.)—The presence of a hydroxyl group in vitamin *E* is demonstrated by its ability to form esters. The acetic or benzoic esters are biologically active, although the methyl and ethyl ethers are inactive. The urethane derivative is inactive, but on alkaline hydrolysis the active vitamin is regenerated. Rats cannot utilise the urethane derivative, although the acetyl and benzoyl esters can replace the vitamin itself. Hydrogenation at 230° C. and at 250 to 280 atmospheres pressure neither destroys the vitamin nor saturates the concentrates. The band at 294$m\mu$, which is found in the absorption spectrum of concentrates from wheat germ and cotton-seed oils, is shown to be uncorrelated with the vitamin.
S. G. S.

Toxicological and Forensic

Biological Methylation of Compounds of Arsenic and Selenium. F. Challenger. (*Chem. and Ind.*, 1935, **54**, 657–662.)—Cases of poisoning due to domestic wall-papers containing arsenical pigments have been known since 1815, and inhalation of arsenic particles, arsine, cacodyl oxide, ethyl arsines, diethyl arsine oxide or monomethyl arsine has been suggested to account for them. Early and current work on the subject is now critically reviewed, and the conclusion is reached that the gas evolved ("Gosio gas") is trimethyl arsine, and that when it reacts with mercuric chloride solution containing hydrochloric acid the compound $(C_2H_5)_2As,HgCl,HgCl_2$ is formed, free calomel being absent (*cf.* Challenger, Higginbottom and Ellis, Abst., ANALYST, 1933, **58**, 235). This conclusion is confirmed by comparison of the m.p. and mixed m.p. of derivatives prepared from Gosio gas and synthetic trimethyl arsine; these include hydroxytrimethyl arsonium nitrate and picrate; trimethyl arsine oxide (produced by the action on the gas of hydrogen peroxide), and its picrate (m.p. 218° to 219° C.); and trimethylbenzyl arsonium picrate, which is prepared by reaction with benzyl chloride. Average yields of trimethyl arsine obtained by allowing bread culture experiments (*loc. cit.*) to proceed until no further precipitate was produced in acid mercuric chloride solution after a week were 22, 24 and 15·5 per cent., with arsenious oxides, sodium methyl arsonate and sodium cacodylate, respectively. They were obtained by weighing the dimercurichloride (*supra*), or the hydroxytrimethyl arsonium nitrate produced by absorbing the gas in nitric acid. No evidence of alkylation was obtained when antimony, sulphur, phosphorus, bismuth, lead or mercury in various forms of combination was substituted for arsenic, but it is recognised that this may occur but not be apparent because of the difficulty in reducing the compound to the gaseous state. Other cases of biological methylation are discussed, *e.g.* the production of odorous compounds by the action of *P. brevicaule* on breadcrumbs containing selenium, or in the breath of animals fed with selenium, tellurium or bismuth compounds; and the conversion of nicotinic acid into trigonelline by dogs (*cf. loc. cit.* and *J. Chem. Soc.*, 1934, 68). In connection with the Forest of Dean case (*cf.* ANALYST, 1932, 57, 163; Lerrigo, *id.*, 155) it is concluded that the cause of poisoning was trimethyl arsine, which is however less poisonous than hydrogen arsenide (*cf.* Huss, *Z. Hyg.*, 1914, 76, 361). The source of the arsenic was the coke-breeze in the plaster on the walls, and the wall-paper was relatively unimportant from this point of view, although this and the adhesive supplied the organic matter necessary for growth of the mould. The danger of the use of coke-breeze slabs for papered walls which are likely to become damp is emphasised. As examples of potential dangers of this nature, 3 patents are cited (Smitt, B.P. 412,091; Stålhane U.S.P. 1,900,690, and Curtin, U.S.P. 1,900,162) concerned with the use of arsenious oxide in wall-boards and in cement to increase its setting rate and insolubility. J. G.

Dermatitis in Relation to Knitted Woollen Goods. S. R. Trotman. (*J. Soc. Dyers and Col.*, 1935, 51, 284–287.)—The difficulties of diagnosing the cause of irritation or dermatitis by woollen garments are discussed, and physical, chemical and micro-biological irritants are considered in turn. (1) *Physical.*—Such agents as sunlight and ultra-violet rays do not concern the hosiery manufacturer directly, but excessive sun-bathing seems to produce changes in the skin, rendering it more susceptible to the action of other irritants or to the growth of micro-organisms. Moreover, the free edges of the epithelial scales of wool may cause irritation or a condition simulating dermatitis. In certain cases where no chemical agent could be found, the garments complained of were made of a coarse wool with well-marked epithelial scales and containing a number of hair-like fibres. (2) Chemical irritants include acids, alkalis, salts, amines, phenols, formaldehyde, dyes, tar oils, nitro-compounds, arsenic and certain vegetable tissues. In order that a chemical may act as an irritant, it must be soluble in moisture, perspiration or skin grease. Woollen underwear which has been stoved and dried without washing may contain as much as 0·5 per cent. of sulphurous acid, as well as traces of sulphuric acid, and very prolonged washing with water is required to remove the acid. With undyed goods, complaints refer almost always to low-grade, stoved wool, fine wools bleached with peroxide rarely causing trouble unless subsequently stoved. As regards dyed wools, the affinity of wool for the residual sulphuric acid, and the difficulty of removing this by washing with water, demand attention. The usual method of rinsing cannot be expected to remove more than a fraction of the absorbed acid, and, unless alkali is used, it is practically impossible to make acid-dyed wool neutral. Formic acid may also be present in dyed woollens. Alkali may be introduced during washing as sodium carbonate, which may undergo hydrolysis yielding a little sodium hydroxide, and the same would occur with residual soap. Tests are described which indicate that the liberation of bases from wool dyes is unlikely to occur. Most of the known pure synthetic dyes are innocuous to the skin, and dye dermatitis is often probably due to unremoved chemicals used as assistants, rather than to the dyes themselves. Skin trouble is, however, set up by chrysoidine, safranine, Bismarck brown, fuchsine, and aurantia. Certain lubricating oils which are used for treating rayon and may contain free fatty acids, vegetable or mineral oil, a hydrogenated aromatic hydrocarbon and sulphonated oil or soap, irritate the hands of those dealing with the goods. Oxidised oils, frequently present in knitted goods, may be irritant, as they contain free fatty acids, hydroxy-fatty acids, aldehydes and peroxides. (3) *Micro-organisms.*—Members of the *Pyogenes aureus* family of cocci, which are widely distributed and often present on the skin, may be the cause of trouble, and are generally associated with the formation of pus. Their rôle is secondary rather than primary, as they do not grow on the skin unless superficial damage has already been effected. Even then, their development is dependent on the general vitality of the infected person. T. H. P.

Agricultural

Palatibility and Possible Toxicity of different Species of *Crotalaria*. R. B. Becker, W. M. Neal, P. T. D. Arnold and A. L. Shealy. (*J. Agric. Res.*, 1935, **50**, 911–922.)—Four species of *Crotalaria* are known to be toxic to live stock, but the toxic principles vary, producing different symptoms and lesions; *C. sagitallis* causes "Missouri River bottom disease," resulting in death among horses; seeds of *C. juncea* L. fed to sheep may cause death; *C. burkeana* Benth. causes death among cattle; and *C. dura* is also definitely toxic. In this investigation nine species of *Crotalaria* were planted in adjacent rows in a fenced 2-acre field, and from time to time during the grazing season two head of cattle were transferred to the field, usually for 14 days, and the extent of the grazing on the separate species was noted. No supplementary feeds were allowed, water was accessible, and some grasses and plants not killed by cultivation were grazed. Eight of the 11 species of *Crotalaria* were dried and fed as hay. It appears that eight of the ten species are not toxic; *C. anagyroides* H.B.K.; *C. goreensis* Guill. and Perr.; *C. grantiana* Harvey; *C. incana* L.; *C. intermedia* Kotschy; *C. lanceolata* E. Mey; *C. maxillaris* Klotzsch; *C. striata* D.C.; and *C. usaramoensis* Baker. *C. spectabilis* Roth is definitely toxic, and one acute and three chronic cases of poisoning by this species are discussed and typical lesions are illustrated. D. G. H.

Quantitative Relationship between the Constitution and Toxicity of some Rotenone Derivatives. W. A. Gersdorff. (*J. Agric. Res.*, 1935, **50**, 893–898.)—The comparison of toxicity of the eight rotenone compounds was made by means of the minimum product of concentration and survival time, the value corresponding with a point at which neither tolerance factor is preponderant. Tests were made with goldfish at a temperature of 27° C., and the following relative toxicities were found:—Dihydrorotenone, 1·4; rotenone, 1·0; acetyldihydrorotenone, 0·81; acetylrotenone, 0·55; dihydrorotenolone, 0·15; rotenolone, 0·097; acetyldihydrorotenolone, 0·082; and acetylrotenolone, 0·055. Each change in chemical constitution was found to effect a change in toxicity independent of the effect of any other change, and the combined effect on toxicity of more than one change in constitution was equal to the product of the individual effects; *e.g.* the dihydroacetates have 0·83 of the toxicity of the parent compounds; the dihydrohydroxy derivatives, 0·15; the acetylhydroxy derivatives have 0·057 the toxicity of the parent compounds, and acetyl hydrorotenolone (which includes all three changes in constitution) 0·082 the toxicity of rotenone. Dihydro derivatives obtained by saturation with hydrogen of the double bond in the side chain have 1·5 times the toxicity of the corresponding unsaturated compounds; the acetates (both the enol type and acetyl derivatives of hydroxy compounds) have 0·56 the toxicity of the parent compounds, and the hydroxy derivatives have 0·10 the toxicity of the parent compounds. D. G. H.

Soya-bean Proteins. M. Mashino. (*J. Soc. Chem. Ind.*, 1935, **54**, 236–238T.)—Methyl alcohol is the most suitable solvent for the extraction of carbohydrates and substances responsible for the characteristic odour, taste and colour of soya-bean oilcakes, a total extract of 11·49 per cent. (carbohydrates, 9·73; crude oil, 0·06; and nitrogen, 0·32 per cent.) being obtained. Additions of water increase the yields of extract progressively, and the use of 0·02 *N* hydrochloric acid in 60 per cent. methyl alcohol prevents the dispersion of the protein, which normally occurs in the presence of water (total extract, 20·00; crude protein, 15·19; ash, 2·81; other substances, 1·99 per cent.). The residue after extraction with benzene and methyl alcohol is a non-hygroscopic, odourless, almost white solid. The greatest yields of oil were obtained at 40° to 50° C. from mixtures of 46, 48 and 50 per cent. by wt. of methyl alcohol in petroleum spirit, b.p. 60° to 70°, 70° to 80°, and 80° to 90° C., respectively. The expression $(125-T)/0{\cdot}71$ gives the percentage of hydrocarbon in the azeotropic mixture in terms of its average b.p. (T); separation into 2 layers does not occur if T exceeds 104° C. The solvents form one layer during extraction, and subsequently separate, at room temperature, into a petroleum spirit layer containing mainly oil, and an alcohol layer containing carbohydrates, phosphatides and colouring matters. The residue contains about 60 per cent. of proteins, and appears to be a suitable raw material for bread or biscuits. Pre-treatment with superheated steam does not greatly affect the rate of decomposition by hydrolysis of the protein contained in the residue after extraction. The liquid obtained after hydrolysis with 25 per cent. sulphuric acid was neutralised with barium hydroxide and concentrated under reduced pressure to obtain the tyrosine, the resulting filtrate being extracted with *n*-butyl alcohol for 97 hours. Arginine, histidine and lysine were then precipitated from the extract by phosphotungstic acid and isolated as picrolonate, picrolonate and picrate, respectively; dibasic acids were not extracted, leucine and phenylalanine were obtained from the soluble portion of the extract, and proline from the insoluble portion. The following average figures show the distribution of the nitrogen in soya-bean proteins:—Amide, 9·58; humin, 6·14; cystine, 1·74; arginine, 15·55; histidine, 7·03; lysine, 6·08; monoamino, 49·19; non-amino, 5·19; diamino, 30·40 per cent. An ethereal solution of the methyl esters of the amino-acids produced after hydrolysis with 38 per cent. hydrochloric acid yielded on evaporation an unknown substance $C_{10}H_{16}O_8$ as monoclinic crystals, m.p. 78° C., soluble in water, methyl alcohol or benzene, and slightly soluble in ethyl alcohol. The following percentage yields of crystalline glutamic acid hydrochloride were obtained before and after acid hydrolysis, respectively, in the presence of the carbohydrates mentioned:—Glucose, 36·51, 60·43; fructose, 54·45, 62·79; sucrose, 35·58, 48·85; starch, 44·94, 61·40; none, 75·06. These figures explain why soya-cake is not used as a source of glutamates, although 40 to 45 per cent. thereof consists of protein containing about 20 per cent. of the acid; 96 per cent. yields are, however, obtainable in the laboratory from cakes which have been extracted with methyl alcohol. The solubility of soya-bean protein at 30° C. in alkali and in solutions of various electrolytes, is "affected" (decreased ?) by heat pre-treatment (at 120° C.), but not by extraction with solvents. Adhesives prepared from soya-protein by treatment with 0·2 per cent. sodium hydroxide solution, followed by coagulation with 0·5 per cent. sulphuric acid, had a lower Amsler shearing strength than similar casein products, unless they were prepared by extraction with the azeotropic mixture of solvents (cf. *supra*), when the strengths were the same. Similar differences were obtained with water-paint products for the solubility and surface produced after drying, and for the hardness and transparency of condensation products with formaldehyde. J. G.

Organic

Ethylene Glycol Monoacetate as a Selective Solvent for the Separation of Paraffins from other Oils. K. B. Edwards and R. Lacey. (*J. Soc. Chem. Ind.*, 1935, 54, 253–254T.)—Ethylene glycol monoacetate is now produced commercially as a colourless, inert almost odourless liquid, of sp.gr. 1·109 at 15° C. It is soluble in water, and when used as a solvent it enables the solute to be recovered by dilution with water, and it therefore serves for the separation of both the soluble and insoluble portions of a mixture. All high-temperature carbonisation creosotes are soluble, whilst the solubility of petroleum and paraffin products decreases with increasing b.p.; the solubility of kerosene is 0·5 to 0·7 per cent. (spindle oils, 0 to 0·25 per cent.). The optimum concentration for use with tar oils and light lubricating oils is 8 vol. of solvent to 1 vol. of oil, and it is convenient to use flasks with graduations on the neck between 80 and 90 ml., the mixture being shaken very vigorously and the readings taken after a settling-period of at least 12 hours. Experiments with synthetic mixtures of anthracene oil and 25 to 90 per cent. of spindle oil showed that, if the solubility-factor is known, very accurate results are obtainable. Down to 2·5 per cent. of petroleum oil in anthracene oil may be detected and determined with an accuracy exceeding that of any other known method; the sp.gr. of the anthracene oil after recovery was 1·084 (1·089 originally). Phenols and acids should first be removed, as large quantities of the former invalidate the test, and as aromatic hydrocarbons separate with the paraffin, the method cannot be used for mixtures of low b.p. petroleum products with benzene, toluene or naphtha. Satisfactory results are obtained for the detection of low-temperature carbonisation in admixture with high-temperature products, since the former contain paraffins. These paraffins may also be separated and examined, but they cannot be differentiated with certainty from the paraffins contained in petroleum, although the sp.gr./b.p. curve method (Edwards, *id.*, 1924, 43, 143T) enables the proportions of high and low-temperature carbonisation products to be estimated. Possibilities also exist in connection with other types of oils; *e.g.* most American pine oils are soluble, whilst Russian oils are not. J. G.

Determination of Urushiol in Lacquer. V-VI. S. Hirano. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 307B.)—The method of determining urushiol by polymerisation with sulphuric acid, whereby a 90 per cent. yield of substances insoluble in a mixture of alcohol and benzene is obtained, yields consistent results only when pure samples are taken direct from the trees, and if oil (*e.g.* perilla oil) has been added to the lacquer, the following adaptation of the method should be used. The lacquer is extracted with absolute alcohol, and to 0·2 g. of the extract and 0·5 g. of paraffin is added 1 ml. of absolute alcohol containing 2 ml. of concentrated sulphuric acid per 100 ml. The alcohol is evaporated, the flask is kept at 100° C. for 30 minutes, and the film formed is treated in the usual way. The percentage of urushiol is obtained by multiplying the figure for insoluble matter by 1·1. Urushiol cannot be determined in a finished lacquer by titration with baryta, since the acid value decreases in the finished product. No such drawback attends the polymerisation method, which gave fairly consistent results. The polymerisation should be carried out at 110–115° C., to ensure all alcohol being expelled. (*Cf.* ANALYST, 1935, 572.) D. G. H.

Inorganic

α-Naphthoflavone as an Indicator for Bromate Titrations. E. Schulek. (*Z. anal. Chem.*, 1935, **102**, 111–113.)—The reagent may be applied as an indicator in the volumetric determination of arsenic or antimony. The solution, containing 5 ml. of strong sulphuric acid in a total volume of 30 ml., is treated with 0·2 g. of potassium bromide and 2 drops of a 0·5 per cent. solution of naphthoflavone in 96 per cent. alcohol. The liquid is titrated with potassium bromate solution until the faint green opalescence changes to a decided rust-brown colour; at the equivalence point the bromo-substitution product flocculates. The reaction is reversible, the colour disappearing on addition of the necessary quantity of arsenious or antimonious salt solution. In the determination of antimony, the liquid should contain 0·5 g. of tartaric acid. Hydrochloric acid in substantial quantity (over 5 per cent.) decreases the sensitiveness of the indicator.

W. R. S.

Volumetric Determination of Manganese by Conversion into Manganic Salt. R. Lang. (*Z. anal. Chem.*, 1935, **102**, 8–16.)—The process is based on induced oxidation of manganous to manganic salt by dichromate in presence of arsenite in metaphosphoric acid solution, and titration of the manganic salt with ferrous sulphate; it follows the lines of the author's method for the determination of cerium (ANALYST, 1934, **59**, 646). The same dichromate, arsenite, ferrous sulphate solutions, and diphenylamine indicator are used. The manganous solution must be free from chloride, but may contain 5 to 40 ml. of strong sulphuric, or 10 to 50 ml. of strong nitric, acid free from nitrous oxides; it is cooled to room temperature, and treated with a solution of metaphosphoric acid in 20 to 25 ml. of water. After addition of 0·1 ml. of indicator, it is treated first with dichromate, then with an excess of arsenite, solution. The following quantities of reagents are used:

For 0·08 g. Mn	HPO$_3$ 5 g.,	K$_2$Cr$_2$O$_7$ 35 ml.,	As$_2$O$_3$ 40 ml.
,, 0·2 ,, ,, :	,, 8 ,,	,, 60 ,,	,, 65 ,,
,, 0·25 ,, ,, :	,, 10 ,,	,, 75 ,,	,, 80 ,,

The red solution is titrated with ferrous sulphate solution, the colour changing to violet, blue, and, finally, grass-green. Other metals do not interfere, with the exception of tungsten, which prevents a sharp end-point when the volume of dichromate solution required exceeds 30 ml. In presence of ferric salt the addition of metaphosphoric acid must be increased, one part of iron requiring ten of the acid. The process is suitable for iron alloys and special steels containing chromium and cobalt. The following quantities are recommended, (1) for metal with less than 5 per cent. of manganese, (2) for metal with more than 5 per cent., and (3) for ferromanganese:

(1)	0·6 g. alloy:	HPO$_3$ 10 g.,	K$_2$Cr$_2$O$_7$ 30 ml.,	As$_2$O$_3$ 35 ml.
(2)	0·4 ,, ,, :	,, 12 ,,	,, 60 ,,	,, 65 ,,
(3)	0·3 ,, ,, :	,, 12 ,,	,, 70 ,,	,, 75 ,,

W. R. S.

Determination of Caesium as Iodobismuthate. R. W. Feldmann. (*Z. anal. Chem.*, 1935, **102**, 102–108.)—The work of Tananaeff and Harmasch (Abst., ANALYST, 1932, **57**, 672) was submitted to critical re-examination. In spite of various modifications in the procedure, which are set out in this paper, the author was unable to effect a recovery of more than 94 per cent. of the caesium taken; the filtrates from the iodobismuthate gave a positive reaction for caesium. Further, it was found that rubidium is precipitated to a certain extent; test separations of caesium from rubidium yielded products containing 7 to 10 per cent. of rubidium in terms of the chloride. It is concluded that the proposed method cannot be described as accurate. W. R. S.

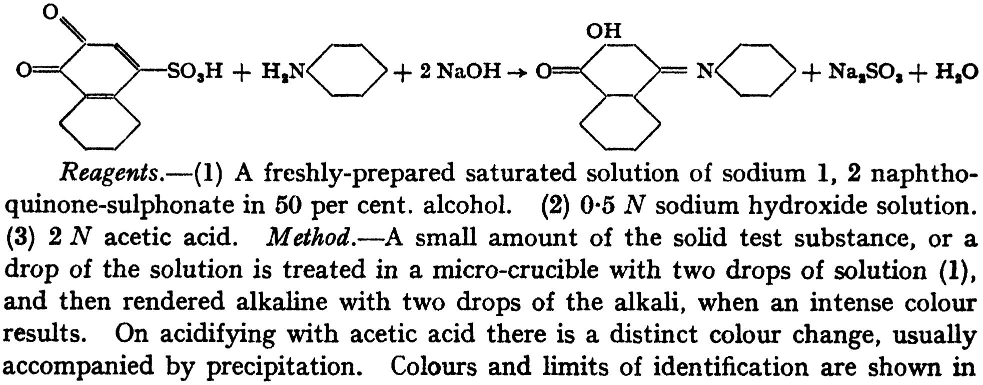
Volumetric Determination of Boron Nitride. B. Ormont and A. Ssamoilow. (*Z. anal. Chem.*, 1935, **102**, 20–24.)—The process, which is based on the conversion of the nitrogen into ammonia, utilises fusion with potassium hydroxide at low temperature in a porcelain crucible in a stream of moist hydrogen. The material (0·05 to 0·1 g.) is weighed in the crucible in a closed weighing bottle. Dry potassium hydroxide (5 to 6 parts) is added, and the crucible is introduced into a wide test-tube closed with a two-holed stopper and placed in a small electric furnace. The stopper carries two tubes bent at right angles; a longer one for the admission of hydrogen, reaching down into the crucible, and a shorter exit tube connected with a conical receiver containing a known excess of standard acid and a little phenolphthalein. Since complete decomposition of the nitride requires 2 hours or more at 250° to 300° C., the receiver is so constructed that a few drops of standard acid can be blown into the knee-bend of the exit tube during a momentary interruption of the hydrogen current. When this is turned on again, any ammonia carried over will colour the indicator after a few minutes. When decomposition is complete, heating is continued for another 15 minutes; the receiver is withdrawn, the tube rinsed through, and the excess of acid is measured with standard alkali.

W. R. S.

Detection of Japanese Acid Clay by the Colour Reaction of Benzidine Solution. K. Kobayashi and H. Ishikawa. (*J. Soc. Chem. Ind. Japan*, **1935**, **38**, 308–309B.)—Owing to the powerful adsorption properties of Japanese acid clay, this clay may be distinguished from ordinary kaolinitic clays by several reagents, and particularly by a solution of benzidine in alcohol. Dried clays should be treated with a 0·05 per cent. solution of benzidine in 50 per cent. alcohol, and wet clays with a 0·1 per cent. solution, when Japanese acid clay will develop an intense blue or greenish-blue colour, whilst no colour develops with kaolinitic clays, even after several hours. D. G. H.

Microchemical

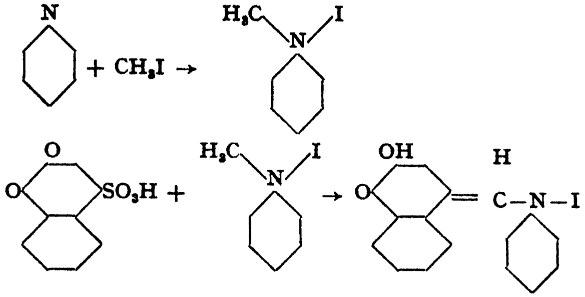
Spot Tests for Organic Compounds (VII) Tests for CH_2– and NH_2– Groups. F. Feigl and O. Freyden. (*Mikrochem.*, 1935, **16**, 79–86.)—The test utilises the reaction between 1, 2-naphthoquinone-4-sulphonic acid in alkaline solution and CH_2– and NH_2– compounds with a replaceable hydrogen atom, giving deeply-coloured quinonoid condensation products:



Reagents.—(1) A freshly-prepared saturated solution of sodium 1, 2 naphthoquinone-sulphonate in 50 per cent. alcohol. (2) 0·5 *N* sodium hydroxide solution. (3) 2 *N* acetic acid. *Method.*—A small amount of the solid test substance, or a drop of the solution is treated in a micro-crucible with two drops of solution (1), and then rendered alkaline with two drops of the alkali, when an intense colour results. On acidifying with acetic acid there is a distinct colour change, usually accompanied by precipitation. Colours and limits of identification are shown in the table.

Compound	Identification limit γ	Colour		Remarks
		With alkali	With acetic acid	
Ethyl malonate	1·2	Deep violet	Yellow and yellow ppt.	—
Rhodanine	0·6	Dark blue-violet	Red-yellow ppt.	—
Ethyl acetoacetate	1·2	Blood-red to violet	Yellow and yellow ppt.	Slow reaction
Thiocyano acetic acid	0·6	Red-brown	Orange	—
Dibenzoyl methane	12	Red-violet	Yellowish-white ppt.	Very slow
m-Nitraniline	6	Yellow-brown	Carmine ppt.	Allow to stand
Benzylamine	0·6	Green	Brown-red	—
Semicarbazide	0·6	Orange-red	Light yellow	—
Aniline	0·12	Auburn red	Light orange	—
β-Naphthoquinoline methiodide	1·2	Dark violet to blue-green	Yellow-brown ppt.	—
β-Napthylamine	0·6	Yellow-red or brown	Carmine ppt.	—
Indole	0·6	Green	Violet	—
Piperidine	0·6	Red	Light-red ppt.	Intense colour reaction without alkali
Pyrrole	0·6	Dark violet	Olive-green	Intense colour

The same reaction may also be utilised for the detection of tertiary ring bases after their conversion into quaternary compounds with methyl iodide or dimethyl sulphate:



Reagents.—(1) Methyl iodide or dimethyl sulphate. (2) Same as (1) above. (3) Same as (2) above. (4) *N* acetic acid. *Method.*—A small amount of the test solution or solid is mixed in a micro-crucible with 5 or 6 drops of methyl iodide or dimethyl sulphate and heated to gentle boiling over an asbestos plate. Some substances very difficult to convert must be heated with the methyl iodide for some hours in a sealed capillary tube in a boiling water-bath. The test is then carried out as described above. The following table shows a number of compounds tested:

Compound	Identification limit γ	Colour		Remarks
		With alkali	With acetic acid	
Pyridine	12	Red to violet	Orange	—
α-Picoline	12	Dark blue-violet	Yellow	—
Quinoline	25	Brown to black-green	Red	—
Quinaldine	12	Violet to blue-green	Greenish-yellow	—
α-6-Dihydroxypyridine-4-carboxylic acid	25	Dark green	Red striations then green ppt.	Use CH_3I
Dimethylpyrone	25	Brown-violet, turning green	Red coloration then ppt.	—
Chelidonic acid	25	Dark green	Red	Use CH_3I
o-Nitraniline		Yellow-green ppt.		$(CH_3)_2SO_4$
p-Nitraniline		Dark green		,,
Atophan		Milky ppt., turning orange	Yellow	CH_3I in sealed tube
Cinchonine	100	Red	,,	,, ,,
Papaverine		Violet-brown ppt., turning orange on standing	,,	,, ,,

J. W. M.

Crystal Formation by "Salting out." L. Rosenthaler. (*Mikrochem.*, 1935, **16**, 37–44.)—"Salting out" is used to precipitate the alkaloids from pharmaceutical preparations. A drop of an approximately 1 per cent. solution of the preparation is put on a microscope slide, and sufficient of the salt for a little to remain undissolved is added. The drop is then covered with a cover-slip, and the crystal formation is observed under the microscope. The following table shows the salts used and the concentration limits when crystals were formed:

	Sulphates of			Chlorides of			Nitrates of		
Test substance	Ammonium	Potassium	Sodium	Ammonium	Potassium	Sodium	Ammonium	Potassium	Sodium
Aconite nitrate	1:1000	—	—	—	—	1:200–1:300	1:750–1:1000	1:200–1:300	1:750
Alipine hydrochloride	—	—	—	—	—	1:100–1:200	1:100–1:200	—	1:750
Apomorphine ,,	1:1000–1:1500	1:200–1:300	1:500–1:750	1:2000	1:2500	1:4000	1:1500	1:1500	1:7000
Berberine ,,	1:4000	1:200–1:500	1:200–1:500	1:10,000	1:2500	1:8000	1:5000	1:10,000	1:5000
Brucine sulphate	1:5000	1:100–1:200	1:750	1:100–1:200	1:200–1:300	1:500–1:1000	—	1:200	1:100–1:200
Quinidine ,,	1:1500–1:2000	1:200–1:500	1:750	1:750	1:2000	1:2500	1:500–1:750	1:750–1:1000	1:2000
Quinine ,,	1:3000	1:1000	1:3000	1:500	1:1000	1:1000	1:300	1:500–1:750	1:1000
Cinchonidine ,,	1:1500	1:200–1:500	1:750	1:200–1:500	1:500	1:1000	1:200–1:500	1:200–1:500	1:750
Cinchonine ,,	1:1000	1:100–1:200	1:200	1:300–1:500	1:1000	1:1000	1:200	1:200	1:1000
Codeine phosphate	1:500	—	—	—	1:100–1:200	1:100–1:200	—	—	1:100–1:200
Caffeine	1:5000	—	1:300	—	—	1:100–1:200	—	—	—
Caffeine sodium benzoate	1:1000	—	—	—	—	—	—	—	—
Diocaine hydrochloride	1:3000 (amorphous)	—	1:500 (amorphous)	1:1500	1:1500	1:3000 (amorphous)	1:2000 (amorphous)	1:2000 (amorphous)	1:2000 (amorphous)
Eucaine A ,,	1:500	—	—	1:300	1:300	1:750	1:500	1:300–1:500	1:1500
Eucaine B ,,	1:750	—	—	1:100–1:200	1:400	1:3000	1:100–1:200	1:100–1:200	1:500
Larocaine ,,	1:250–1:500	—	—	—	—	1:250–1:500	1:100–1:200	—	1:250–1:500
Morphine ,,	—	—	—	—	—	1:200	—	—	1:200
Novocaine ,,	(amorphous)	—	—	—	—	1:100	—	—	(amorphous)
Panthesin	1:1000	1:100 (amorphous)	—	—	1:200	1:750	1:300–1:500	1:200	1:1000
Psicaine hydrochloride	1:500–1:1000 (amorphous)	—	—	1:500–1:1000	1:500–1:1000	1:1500	1:500–1:1000	1:500–1:1000	1:2500
Aminopyrine	1:1000	—	1:200	—	1:200	1:250–1:500	—	—	1:250–1:500
Stovaine hydrochloride	—	—	—	—	—	1:100–1:200	—	—	1:200
Strychnine ,,	1:1500	—	1:200–1:400	1:500–1:1000	1:1000–1:2000	1:1000–1:2000	1:200–1:400	1:200–1:400	1:500–1:1000
Atropine									
Hexamethylene tetramine	—	—	—	—	—	—	—	—	—
Antipyrine	1:100 (drops only)	—	—	—	—	—	—	—	—
Emetine hydrochloride	1:100 (amorphous)	—	—	1:100 (amorphous)	1:100 (amorphous)	1:100 (amorphous)	1:100 (amorphous)	1:100 (amorphous)	1:100 (amorphous)

J. W. M.

Physical Methods, Apparatus, etc.

Standardisation of Photochemical Methods for the Measurement of Solar Ultra-violet Radiation. H. S. Mayerson. (*Amer. J. Hygiene*, 1935, 22, 106–136.)—The acetone and methylene blue method (Webster, Hill and Eidinow, *Lancet*, 1924, 1, 745), the zinc sulphide method (Clark, ANALYST, 1929, 54, 493), and the oxalic acid method (Anderson and Robinson, *J. Amer. Chem. Soc.*, 1925, 47, 718) for the measurement of solar ultra-violet radiation have been calibrated against a radiometric (thermopile-screen) method, and are now compared. The first method is the simplest and most convenient and, being slow, it requires little attention. However, it gives only approximate results, because the reaction is reversible in the dark; the temperature-coefficient (1·25 per 10° C. rise) is high, and the correction is difficult to apply; the rate of bleaching is not uniform and decreases as the reaction proceeds; and the maximum sensitiveness is to light of wave-length below 270*mμ*, which is absent from solar radiations. Methods for controlling these errors are suggested. The reaction is sensitive to visible radiation between 570 and 710*mμ*, and it is suggested that 700 ergs per square cm. per second should be taken as the antirachitic energy shorter than 313*mμ* required to bleach the standard acetone and methylene blue solution by 1 unit in 1 hour; that radiations should always be measured at normal incidence; and that the bleaching due to the visible spectrum should be determined by simultaneous exposure of a glass control tube and an allowance made. The zinc sulphide method is simple, rapid and convenient, so long as apparatus for making accurate measurements of reflection factors is available, since colour-charts are unsatisfactory. It is irreversible and is sensitive only to ultra-violet radiation (and particularly to the antirachitic constituents); under the conditions specified the change observed is proportional to the intensity of the radiation. It is suggested that "green glass" slides should be used to isolate the radiations of wave-lengths below 313*mμ*, and that in correcting for the difference between the readings obtained in quartz and glass vessels the difference value should be reduced by the factor 0·13. Disadvantages are the variations in the sensitiveness of different batches of zinc sulphide, and the changes in colour which they undergo on storage in the dark. One unit, for wave-lengths of 290 to 350*mμ*, is equivalent to a radiation intensity of 735,000 ergs per square cm. The oxalic acid and uranyl sulphate method is in all respects the most desirable. The apparatus is simple, the reagents are readily available in the pure state, and the final result is obtained by means of a standard accurate titration. Unless allowance is made for radiation from the sky, measurements of solar radiation at normal incidence are not comparable, and this difficulty may be overcome by means of a blank test (cf. *supra*), or by an arrangement of black metal discs with concentric openings. The intensity of radiation, as measured by this method, may be expressed in ergs per square cm. per second by multiplying the number of mg. of oxalic acid decomposed per sq. cm. in 30 minutes by 18,300 (for wave-lengths between 290 and 390*mμ*). The reaction depends on the decomposition of 0·1 *N* oxalic acid in the presence of a 0·01 *N* solution of uranyl sulphate as a photosensitiser; Moss and Knapp (*J. Soc. Chem. Ind.*, 1935, 44, 453T), however, recommend uranium acetate. The liquid is exposed in a quartz cell, 1·5 to 2 cm. thick (or in a glass cell with a Corex glass face), and the oxalic acid is titrated with 0·1 *N* potassium permanganate solution; the unit is the number of mg. of oxalic acid decomposed per unit time per square cm. of surface exposed. The amount of decomposition is directly proportional to the intensity of the radiation, so long as not more than 50 per cent. of the oxalic acid is decomposed. The absorption of the solution does not change materially during prolonged exposure, and variations due to differences in temperature are negligible. To facilitate intercomparison of data obtained in different localities by different methods, it is suggested that all results should in future be expressed in absolute units by means of the factors given. J. G.

Reviews

CHEMISCHE GRUNDLAGEN DER LEBENSVORGÄNGE. Eine Einführung in biologische Lehrbücher. CARL OPPENHEIMER. Pp. vii + 298. Leipzig: Georg Thieme. Price R.M. 22·50.

The increasing refinements of analytical methods have had a profound influence on biochemical theory. At the beginning of this century most biochemical textbooks opened with a bold statement that "protoplasm" was built up from carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorus. By slight stretching of the imagination, iron, calcium, sodium, potassium and magnesium were also included among the biologically essential elements. To-day, following on the development of analytical technique which has allowed of the determination of smaller and smaller quantities, it is realised that copper, manganese and iodine must also be included in the list. Barium, zinc, arsenic, aluminium, bromine and fluorine are almost invariably present in living tissues, but whether as essential or incidental factors is not fully known. The same can be said of the long list of elements found, by spectroscopic methods, freely distributed in the tissues of marine animals.

Professor Oppenheimer's book sums up present knowledge of the elementary composition of living matter and gives a broad review of the working of the chemical machine. He takes up the position that no sharp line is to be drawn between chemical combination and adsorption, or between the substance of the life-machine and the other constituents that are required to keep it working. He devotes a section to the chemical components of living matter, and others to the processes of metabolism and to catalysts and enzymes, with particular attention to the problem of cell oxidation. A section on the energetics of living matter brings to an end a book which is well balanced and well written and full of interest on every page. DOROTHY JORDAN LLOYD

THE APPLICATION OF ABSORPTION SPECTRA TO THE STUDY OF VITAMINS AND HORMONES. R. A. MORTON. Pp. 70. With 6 plates. Adam Hilger, Ltd. 1935. Price 10s. net.

Since the days of Bunsen, spectroscopy has been, in a sense, part of the analyst's territory; it may, however, be considered to have been given *de jure* recognition at the Society's meeting on 7th November last. Dr. Morton's monograph, though it covers only part of the domain, has nevertheless a double appositeness, for members of the Society are becoming increasingly involved in the physical and chemical methods of estimating vitamins, hormones and other substances first recognised and measured by their physiological activity.

In his 66 pages Dr. Morton has been able to outline the relevant researches that have led to the present position and to define that position in some detail and with the necessary qualifications, which are laid down in a commendably accurate manner. He makes it clear that spectrophotometric assay is the most accurate method available for measuring vitamin *A*, in most natural sources, provided steps are taken to estimate any significant quantities of carotene that may also be present; that it is an essential part of any attempt to assess the purity of calciferol, the crystalline artificial vitamin *D*; that its possibilities in the determination of vitamins B_1 and *E* are worthy of further exploration; that the peculiar properties of ascorbic acid (vitamin *C*), in that its ultra-violet spectrum changes with *p*H, render its spectrometric examination of analytically diagnostic value; and that the possibilities of its use in hormone bio-chemistry are by no means to be ignored.

All the known substances comprised under the terms hormones and vitamins, except the "flavins," are colourless, or nearly so, and it therefore follows that the methods of ultra-violet spectroscopy and spectrophotometry are alone in question; with the great improvements effected in this technique during the last two decades —improvements towards which the publishers of this book have contributed very largely—this use of the invisible spectrum to-day involves substantially no more serious problems of method and equipment than does the use of the visible.

It is to be hoped and expected that more than one edition of Dr. Morton's interesting and lucid exposition will be called for. When it is, we trust that the opportunity will be taken to eliminate the rather manifold signs of haste in production from which it must be admitted to suffer. There is evidence of inadequate proof-reading, which has led to the appearance on p. 28 of a structural formula for vitamin *A* that is not only wrong, but impossible, to the writing of "inactive" for "active" on p. 7 (par. 3, line 5), to an incorrect "legend" to figure 3 (p. 14), to the omission of the essential words "for the oil" from the beginning of line 3 on p. 24, to the appearance of "Fig. 20" under two different diagrams (pp. 51 and 57; the second should be "Fig. 21"), and to certain minor "literals."

In his quite legitimate anxiety to take into account the most recent work Dr. Morton has, on p. 12, summarised the evidence that makes the existence of vitamin *D* in more than one form very probable; unfortunately this completely invalidates the statement made seven pages earlier, that *calciferol* circulates in the blood-stream after irradiation of the animal organism. We simply do not know which of the several possible forms of "vitamin *D*" is natural to man and other mammals. Any new edition will, doubtless, be able to carry the story of vitamin *D* some stages further; there is at present quite a vigorous controversy raging between the experts on the nature of the chemical changes following the irradiation of ergosterol, and consequently on the precise constitution of calciferol.

Again, it is surely not legitimate for Dr. Morton, or anyone else, to depart from factors having the international sanction of the Permanent Commission on

Biological Standardisation, unless he makes it abundantly clear that he has done so. Dr. Morton gives the biological activity of pure vitamin *A* as 1·8 million international units per gram (pp. 22 and 26), and the factor for converting $E^{1\%}_{1\,\text{cm.}}$ 328$m\mu$ to international units as 1100; the figures fixed by the conference of June, 1934, were 2·56 million and 1600, respectively. The work on which Dr. Morton obviously bases his departure from these figures was presented by himself and Mr. R. S. Morgan to the Biochemical Society early this year; but, though this work has just been published, Dr. Morton is likely only to confuse the unwary by making this departure without anywhere stating that he has done so.

The list of carotenoids and related substances, with their more important properties (Table III, pp. 31–33), is a valuable feature of this book, and should be sufficient by itself to recommend it to plant chemists. Doubtless any new edition will see a considerable extension of this list, which might then be printed across two pages, with an extra column for stating the known more important sources of each substance; in this edition no source is given for several of them.

Although we have criticised above a number of inaccuracies and mis-statements, most of which are, we suggest, simply due to haste in production, the selection of facts in this book and their method of presentation are such as to make it quite clear that any future edition will not be allowed to lag behind current research. Dr. Morton is to be congratulated on the precision with which he has, in general, defined and carried out his survey, but it might be suggested to the publishers that the cost is somewhat excessive for 70 pages of even so excellent a piece of work; it seems quite likely that its sale might be trebled or quadrupled if the price were halved.

A. L. Bacharach

A German-English Dictionary for Chemists. By Austin M. Patterson, Ph.D. Second Edition. Pp. 411. London: Chapman & Hall. 1935. Price 15s. net.

The first edition of this useful little handbook was published in 1917, and has been repeatedly reprinted. The fifth (1924) issue, which contained 27 pages of addenda, was reviewed in The Analyst (1925, **50**, 260), and now we have a revised second edition in which the supplementary pages have been incorporated in the body of the book, and a large amount of new matter has been added. During the years that have passed since the last revision there have been great changes of concept in chemistry, especially in chemical physics, with a corresponding coinage of new words. Most of these will be found in this new edition, which now comprises some 42,000 entries, and has 68 more pages than its predecessor, notwithstanding the fact that some space has been gained by omission of numerous words that are rarely met with in technical literature.

In revising the dictionary Dr. Patterson has consulted not only the standard scientific and technological dictionaries, but also specialised dictionaries on metallurgy, biology and bacteriology (*e.g.* Partridge's *Dictionary of Bacteriological Equivalents*), and he has succeeded in producing a book that is well nigh invaluable to all who wish to study German chemical publications. In particular, mention should be made of the very large number of abbreviations, with their English equivalents, which have been included; abbreviations such as "ä.W.," "Dz," "Q.S.," and "KZ" are too often a stumbling block to the foreign reader of German technical books.

We can fully endorse all that was said in praise of this dictionary when it was last reviewed. It is clearly printed and singularly free from typographical errors, is in a binding that is easy to handle and, when consulted, will seldom be found wanting.

EDITOR

Annali di Merceologia Siciliana. Vol. II. 1933–1934. Pp. 319. Catania.

In this volume various industries carried on in Sicily and elsewhere in Italy are discussed in turn by different authors. Attention is directed first to cotton, which was introduced into several districts of Italy and into Sicily by the Arabs, probably over 800 years ago. The soil and climate of Sicily are well suited to the growing of cotton, which at one time was carried on there on a considerable scale. In Italy itself the cultivation has been relinquished, but in Sicily, although greatly restricted, it still persists. Now that the spinning and weaving of cotton are being developed in the countries where the main bulk of the raw material is grown, expansion of the cultivation in Sicily, and abolition of the tax on cotton-seed oil, are urged.

An excellent account is given of the citric acid position throughout the world and of the way in which the biological manufacture of the acid has affected what was once virtually a Sicilian monopoly. Other industries discussed are those of sea-salt, sheep-raising, limestone, antimony, tunny fishing, papyrus, and the de-tinning of tinned-sheet scrap. Communications are also included describing a new volumetric method of determining mercuric chloride (by C. Chines), and a densimeter for use with small amounts of liquid (G. Ajon).

T. H. POPE

Cereal Laboratory Methods. Committee of Methods of Analysis, American Association of Cereal Chemists. Third Edition. Pp. vii + 204. American Association of Cereal Chemists, Omaha Grain Exchange, Nebraska. 1935. Price $3.

Those chemists interested in cereal work in England will welcome the third edition of this publication dealing with the methods they normally employ. In general the methods are distinctly American, and but little reference has been given to other accepted methods used by chemists in Europe. It is also a pity that dough-testing methods have not progressed sufficiently or been sufficiently accepted to have been included and described.

The present edition has the following chapters and headings:—I, Wheat and other Whole Grains; II, Feeds and Feeding Stuffs; III, Wheat Flour, Semolina, and Similar Products; IV, Enzymatic, Physico-chemical, and Miscellaneous Methods; V, Baking Tests; VI, Baked Cereal Products; VII, Macaroni Products; VIII, Fats and Softening Materials; IX, Leavening Agents; X, Yeast Foods, Flour Improvers, etc.

The appendix contains a number of useful tables dealing, amongst other things, with the Munson–Walker equivalents for sugar, correction factors for the determination of carbon dioxide, percentage of protein and ash with varying moisture, etc.

Some of the methods deal with aspects of problems with which we are little concerned in this country, and so may not appeal directly to English chemists.

The third edition is undoubtedly arranged in a more attractive manner than the second edition, although it is not much larger. For example, the first chapter on Wheat and other Whole Grains is curtailed and deals only with essentials. Much work on the nature of the proteins present and the like has been cut out, since it really appears under the section on flour and semolina. The chapter dealing with Feeds and Feeding Stuffs consists mainly of methods recommended by the Association of Official Agricultural Chemists.

In Chapter III, full and useful methods are given. It is interesting to note that the Rask method for the determination of starch is given as originally proposed, and that no mention is made of the use of sand, without which, particularly with soft flours, it is sometimes difficult to obtain accurate results. In the estimation of chlorine in flour extraction is advocated with anhydrous alcohol-free ether instead of with the petroleum spirit generally used in England. Similarly, in the chapter on Enzymatic and Physico-chemical Methods, no mention is made, in the description of the determination of maltose, of the procedure by Lane and Eynon with methylene blue, which is common practice in England, especially when this test is used for routine work.

The chapter on Baking Tests is mainly concerned with the standard American baking test employing 100 grammes of flour, which method so far has not commended itself in Europe.

The book will, however, be much appreciated by those chemists in flour mills and bakeries, and others, who are faced with the problems of the analysis of cereal products, as the methods given are clearly described and are, in general, of proved usefulness. The Committee of Methods of Analysis of the American Association of Cereal Chemists, under the chairmanship of C. E. Mangels, is, therefore, to be congratulated.

D. W. KENT-JONES

Publications Received

INORGANIC COLLOID CHEMISTRY. Vol. II. HYDROUS OXIDES AND HYDROXIDES. By H. B. WEISER. Pp. vii+429. London: Chapman & Hall. Price 23s. 6d. net.

PLANT PHYSIOLOGY. By MEIRION THOMAS. Pp. xii+494. London: J. & A. Churchill, Ltd. Price 15s.

SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS. By F. SUTTON. Twelfth Edition. Revised by A. D. MITCHELL. Pp. xvi+631. London: J. & A. Churchill, Ltd. Price 35s.

STRUCTURE AND COMPOSITION OF FOODS. Vol. II. VEGETABLES AND FRUITS. By A. L. and K. B. WINTON. Pp. xiv+904. London: Chapman & Hall. Price 75s. net.

MIKRO-MASSANALYTISCHE BESTIMMUNG DES KOHLENSTOFFES UND WASSERSTOFFES. By J. LINDNER. Pp. vii+374. Berlin: Verlag Chimie G.M.B.H. Price RM. 20.

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AGR. RES.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 2nd, Mr. John Evans, President, being in the chair.

Certificates were read in favour of:—William Reginald Bage, Albert R. Bonham, B.A.Sc. (Toronto), F.C.I.C., Henri Charles Philip Chapleau, B.A.Sc. (Montreal), Leo Cooksey, B.Sc. (Lond.), F.I.C., Douglas Eric Davis, B.Sc. (Lond.), F.I.C., Frederick Ellington, B.Sc. (Lond.), A.R.C.S., A.I.C., Edward Oscar Heinrich, B.S. (California), James Arthur Durham Hickson, B.Sc., A.I.C., Donald Robert Jackson, Daniel Carswell Macpherson, B.Sc. (Edin.), Florence Ellen Murphy, B.Sc. (Lond.), Temple Clifford John Ovenston, B.Sc., Ph.D. (Lond.), A.I.C., George Herbert Stott, M.Sc. (Liverpool), F.I.C., Basil C. L. Summers, B.Sc. (Lond.), Stanley Gordon Willimott, B.Sc. (Liv.), Ph.D. (Liv. and Cantab.), A.I.C.

The following were elected members of the Society:—Francis Highland Milner, B.Sc., A.I.C., Lewis Charles Nickolls, M.Sc. (Lond.), A.R.C.S., D.I.C., A.I.C., Corbet Page Stewart, M.Sc. (Dunelm), Ph.D. (Edin.), and Sidney Lionel Tompsett, D.Sc. (Lond.), Ph.D. (Glas.), A.I.C.

The following papers were read and discussed:—"The Chemical Examination of Furs in Relation to Dermatitis. Part VI—The Identification of Vegetable and other Dyes," by H. E. Cox, D.Sc., Ph.D., F.I.C.; "Testing for 'Sea Water Damage'," by W. M. Seaber, B.Sc., F.I.C.; and "A Contribution to the Iodimetric Titration of Tin," by F. L.Okell, F.I.C., and John Lumsden, B.Sc., A.I.C.

NORTH OF ENGLAND SECTION

A meeting of the Section was held in Manchester on October 12th. The Chairman (Professor W. H. Roberts) presided over an attendance of forty-one.

The following papers were read and discussed:—"Colorimetric Determination by Photo-electric Cell," by N. Strafford, M.Sc., F.I.C.; "The Oxalates of Calcium, Barium, Strontium, and Magnesium," by J. Haslam, M.Sc., A.I.C.; and "Medicines Ancient and Modern," by U. A. Coates, M.P.S.

It was decided to send a letter of congratulation to Dr. J. T. Dunn on his recovery from illness.

ANALYTICAL METHODS COMMITTEE

Sub-Committee on Methods of Soap Analysis

The Sub-Committee which dealt with methods for the determination of Unsaponifiable Matter in Fats and Unsaponified Fat in Soaps, has now been reappointed as a Sub-Committee on Methods of Soap Analysis. The members of this Sub-Committee are Dr. H. E. Cox, F.I.C. (*Chairman*), and Messrs. E. R. Bolton, F.I.C., D. E. Davis, B.Sc., F.I.C., F. R. Ennos, B.Sc., F.I.C., N. Evers, B.Sc., F.I.C. (*Hon. Sec.*), B. D. W. Luff, F.I.C., and W. H. Simmons, B.Sc., F.I.C.

Sub-Committee on the Determination of the Freezing-point of Milk

A Sub-Committee has been appointed to take over the work of the British Standards Institution on this subject. The Sub-Committee consists of:—Mr. A. More, F.I.C. (*Chairman*), and Messrs. E. B. Anderson, M.Sc., F.I.C., G. D. Elsdon, B.Sc., F.I.C., J. Golding, D.S.O., F.I.C., J. A. Hall, B.Sc., A.R.C.S., Prof. J. C. Philip, M.A., D.Sc., F.R.S., and J. F. Tocher, D.Sc., F.I.C.

Obituary

HUGH CHARLES HERBERT CANDY

The second son of the Rev. Herbert Candy, at one time Vicar of Orton, Leicester, Hugh Candy was educated privately and at University College, London, from which institution he graduated B.A. in 1883 and B.Sc. in 1888. His first appointment was as a master at Epsom College, and in 1895 he was appointed Lecturer in Physics and Chemistry at the London Hospital Medical School. He was also appointed Arnott Professor of Natural Philosophy at Queen's College, London. In 1911 he relinquished the teaching of physics at the London Hospital, in accordance with the newly-established regulations of the University, whereby a teacher of the University could only be "recognised" in one subject. Henceforth, therefore, his services were entirely devoted to the teaching and advancement of chemistry.

He was elected a member of the Society of Public Analysts in 1897, and served on the Council in 1909–1910. In 1898 he was elected a Fellow of the Institute of Chemistry and served as a member of the Council from 1916 to 1919.

While from his university education Candy might have been expected to have had equal loyalties to the arts and to science, I have the impression that, although he earned his living by teaching science, and, although he was the author of several standard scientific text-books, one of which—*Manual of Chemistry for Medical Students*, by Luff and Candy—has passed through seven editions, his real interests lay rather with the humanities. My reasons for this opinion are partly his great love of books—he was an indefatigable and discerning book-collector, being the possessor of many first editions of the English classics—and partly because he always, I thought, became more animated when a literary allusion was made than when a scientific problem was discussed. His literary interests and ability were well exhibited in his book published in 1924 on *Some New Discovered Stanzas*, *written by John Milton on Engraved Scenes Illustrating Ovid's Metamorphoses.* Although the attribution of these stanzas to Milton has not received by any means universal acceptance, the arguments advanced by Candy in support of his contention made on many, including so critical a judge as the late Edmund Gosse, as favourable an impression as in the circumstances could be expected.

Not only was Candy a scholar of the old school, belonging to a time when university examinations, and particularly those of the University of London, were more broadly based than they are to-day; he was also indisputably a gentleman of the old school, passing through life with dignity and serenity, and with a never-failing courtesy to all and sundry.

Troubles, and of these he had more than his share—losing a son, the father of a young family, when on the threshold of his professional career, and later a much-loved and gifted daughter—though chastening, entirely failed to embitter him. His philosophy enabled him to ride all the storms of life—the boat swung but the anchor held—and it is pleasing to think of him in the evening of his day living peacefully and quietly in the company of his devoted wife, finding pleasure, as with all his modesty I feel he must have done, in the remembrance of good work well done, and comfort in those literary studies which his early training and cultured taste had taught him to appreciate and enjoy. Life and death being what they are, surely here is no occasion for tears or for beating the breast; rather an occasion for gratitude for so long and useful a life and for so noble an example.

In Cœlo Quies.

William Wright

PERCY ARTHUR WILLIAM SELF

Percy Arthur William Self had been a member of our Society only since 1929, but by his death on May 24th, at the early age of 53, we have lost a chemist of unusual ability and mentality.

Self was a native of Williton in Somerset, and after serving a pharmaceutical apprenticeship in Yeovil, he entered the School of the Pharmaceutical Society in 1904, and completed his "Major" in 1906. He took his London B.Sc. degree in the same year, and became a Fellow of the Institute of Chemistry in 1912.

Shortly after completing his training he commenced work with the late E. F. Harrison, and in the course of a few years joined him as a partner. His work was always of a pharmaceutical character, and his published results indicate what a wide field of research that could cover.

He was a member of the Pharmaceutical Chemistry Sub-Committee of the British Pharmacopoeia Commission, and Chairman of the Pharmaceutical Chemistry Sub-Committee which dealt with the revision of the "Codex." As an examiner to the Pharmaceutical Society and, in pharmacognosy, to London University, his particular knowledge was of great assistance in educational matters, and gained him a wide circle of acquaintances.

His quiet retiring personality will live in the memory of many of his colleagues, but his unobtrusive helpfulness to men who had to leave their duties during the war will be known only to those who benefited by his many kindnesses.

C. E. Sage

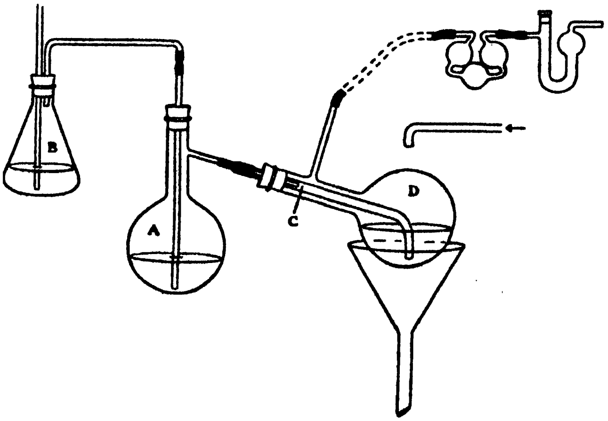
The Determination of Mercury in Viscera

By CLIVE NEWCOMB, D.M., F.I.C., S. RAJAGOPAL NAIDU, M.B., M.Sc., F.I.C.,
AND K. S. VARADACHAR, M.A., M.Sc.

The method previously in use in this laboratory for the determination of mercury in viscera consisted in destruction of organic matter with potassium chlorate and hydrochloric acid and precipitation and weighing of the mercury as sulphide. There are many difficulties inherent in the method, especially when other metals, such as arsenic, iron, bismuth, copper or lead, are also present.

If arsenic is present, the separation of the mixture of the sulphides by means of dilute alkali is liable to peptise part of the mercuric sulphide, so that some of it passes through the filter. If bismuth, copper or lead is present and the mixed sulphides are treated with nitric acid, it is difficult to adjust the strength of the acid so as to dissolve the whole of the bismuth, copper or lead sulphide and none of the mercuric sulphide. The method can be made to work, but requires experience. If iron is present in considerable quantities, some iron sulphide is very likely to be co-precipitated with the mercury, and the last traces of it are difficult to remove.

The method described below relies on the volatility of mercuric chloride. The organic matter is destroyed by means of nitric and sulphuric acids, and the mercury is distilled off from the hot sulphuric acid in a stream of hydrochloric acid gas. At the temperature of boiling, or nearly boiling, sulphuric acid mercuric chloride can be completely distilled off.



A 500-ml. distilling flask, A, is fitted with a cork carrying a straight tube reaching to the bottom of the flask and connected with a wash bottle, B, containing concentrated hydrochloric acid. The side tube of the distilling flask is slipped into a wider tube, C, into which it enters to a distance of about three inches, and is held in position by means of a small piece of rubber tubing slipped over the two tubes. The tube, C, passes through a cork fitted to another 500-ml. distilling flask, D, containing about 300 ml. of distilled water, and is bent down at the end, so that it nearly reaches the bottom. The side-tube of the flask, D, is connected with a potash bulb containing water and then with a Peligot tube also containing water. The other end of the Peligot tube is connected with a suction pump. The flask, D, is kept cool by means of a stream of water.

A suitable quantity of the visceral matter is placed in the 500-ml. distilling flask, A, disconnected from the rest of the apparatus, and concentrated nitric acid is added slowly without heating until a vigorous reaction sets in. As the reaction subsides further quantities of nitric acid are added till digestion is complete, and the whole has become a uniform yellow solution. The flask is then fitted with the cork and tube leading to the bottom of the flask and connected with the absorption part of the apparatus, as shown in the diagram. Suction is begun by the filter pump and about 50 ml. of strong sulphuric acid are added slowly through the long tube. The flask is then heated until white fumes begin to appear inside the flask. Any tendency to char is prevented by adding a few drops of strong nitric acid from time to time. (The current of air passing through the sulphuric acid prevents the fumes from attacking the corks and at the same time hastens the destruction of the organic matter.)

The heating is then stopped, and the contents of the absorption flask, the potash bulb and the Peligot tube are filtered into a beaker. This filtration is necessary to free the solution from small quantities of fatty acids that distil over. The filter is washed, and the washings are added to the filtrate. This liquid, which contains nitric and nitrous acids, is treated with potassium permanganate till pink, to oxidise the nitrous acid, and then decolourised with oxalic acid. Hydrogen sulphide, washed by passing through water, is passed into the liquid and the mercury is precipitated as sulphide. The precipitate, which accounts for about a third of the total mercury, contains a fair amount of sulphur. The precipitate is allowed to settle and the supernatant liquid decanted on to a filter. The precipitate is washed several times with water and the washings decanted on to the filter, the main bulk of the precipitate being retained in the beaker. This is dissolved in bromine water and the solution is poured on to the filter, the filtrate and washings of the beaker and filter being collected in a flask. This bromine solution is kept until a later stage.

A fresh quantity of distilled water is placed in the absorption flask and tubes and the apparatus is re-connected. This time the wash-bottle containing hydrochloric acid is connected with the tube in the distillation flask. Suction and heating are started and continued for three hours. At the end of the period the apparatus is disconnected, and the contents of the absorption flask and tubes are washed into a beaker. The mercury in this solution is precipitated as sulphide, filtered off, washed and dissolved in bromine water, as before. The two bromine solutions are now mixed and boiled till free from bromine. The solution is acidified with hydrochloric acid and the mercury is re-precipitated as sulphide, which is filtered through a Gooch crucible, washed, dried and weighed.

The procedure of dissolving the precipitate of mercuric sulphide in bromine water, filtering, boiling off the bromine and re-precipitating as sulphide is very effective in getting rid of the sulphur, and is preferable to washing the precipitate with carbon disulphide.

The method was first tried with pure mercuric chloride solution, and the following results were obtained:

Mercuric chloride taken, mg. ..	131·0	176·0	169·0	70·0
„ „ recovered, mg. ..	130·0	176·0	167·5	68·6

In these experiments the preliminary destruction of organic matter with nitric acid was omitted.

The method was then tried on viscera to which known quantities of mercuric chloride had been added, with the following results:

Mercuric chloride added, mg. ..	14·5	14·5	20·4	30·0	120·4	120·4	120·4	130·9	130·9	196·4
Mercuric chloride recovered, mg.	14·5	13·8	20·2	30·5	118·8	119·6	119·6	129·2	129·5	194·0

Thus, with quantities up to about 200 mg. of mercuric chloride the method is fairly accurate. With larger quantities the distillation was not completed in three hours. For example, with 550 mg. of mercuric chloride added, only 430 mg. were recovered.

The method was then tried on viscera containing mercury, bismuth, copper, iron and lead, respectively, in addition to mercury, and the following results were obtained:

Mercuric chloride taken mg.	Added metal in solution	Mercuric chloride recovered mg.
150·0	Bismuth	148·5
167·5	Copper	165·0
167·5	Iron	165·0
133·6	Lead	131·6

The method was also tried on mixtures of arsenic and mercury. From inorganic solutions arsenic, if present in the tervalent condition, distils over with the mercury. But, if the arsenic is oxidised to the quinquevalent condition by means of nitric acid before distillation, mercury alone distils over and arsenic is left behind in the sulphuric acid, in which it can be quantitatively determined. Thus an inorganic solution containing both mercury and arsenic, after oxidation with nitric acid and distillation, yielded the following results:

$$\text{Added} \left\{ \begin{array}{l} 31{\cdot}8 \text{ mg. } As_2O_3 \\ 150{\cdot}0 \text{ mg. } HgCl_2 \end{array} \right. \qquad \text{Recovered} \left\{ \begin{array}{l} 30{\cdot}2 \text{ mg. } As_2O_3 \\ 147{\cdot}4 \text{ mg. } HgCl_2 \end{array} \right.$$

With viscera containing both mercury and arsenic, the method of destruction of organic matter employed above converts the arsenic to the quinquevalent condition. Mercury alone distils over and arsenic is left behind in the distillation flask. The results of a determination are given below:

$$\text{Added} \left\{ \begin{array}{l} 31{\cdot}8 \text{ mg. } As_2O_3 \\ 150{\cdot}0 \text{ mg. } HgCl_2 \end{array} \right. \qquad \text{Recovered} \left\{ \begin{array}{l} 30{\cdot}5 \text{ mg. } As_2O_3 \\ 147{\cdot}5 \text{ mg. } HgCl_2 \end{array} \right.$$

The method described above is thus seen to be of advantage in the determination of mercury in viscera, especially in the presence of other heavy metals.

The possibility of a loss of mercury when excess of bromine is boiled off from a dilute mercury bromide solution had previously been investigated by us (cf. *Annual Report of the Chemical Examiner to the Government of Madras*, 1934; ANALYST, 1935, 759), and was further investigated in connection with this paper.

The recovery of nearly all the mercury in this method shows that the loss, if any, cannot be great. The following tests were made:

(i) By distilling the solution of mercuric bromide and bromine until all the colour of the bromine had disappeared and testing the distillate for mercury. It was found that with dilute solutions, up to 1 in 1000 (200 mg. of mercuric chloride in 200 ml. of water), no visible precipitate of mercury sulphide could be obtained from the distillate. With stronger solutions some loss occurred. This loss could be prevented by the addition of potassium chloride to the solution. In one experiment 600 mg. of mercuric chloride were precipitated as mercuric sulphide and dissolved in 200 ml. of water by excess of bromine, 5 g. of potassium chloride were added, and the mixture was distilled. The excess of bromine had boiled off when 10 to 15 ml. had distilled over, but the distillation was continued until 100 ml. of distillate had been collected, and in this no mercury could be detected.

(ii) By testing the final precipitate of mercuric sulphide for sulphur by extraction with carbon disulphide. No loss of weight of the precipitate was caused by this extraction and the carbon disulphide left no residue on evaporation.

To make sure that all the arsenic was retained under the conditions of the method a solution of arsenious oxide in sulphuric acid was oxidised and distilled, as for mercury, by this method. No precipitate was obtained on passing hydrogen sulphide through the distillate, and the Reinsch test was negative.

CHEMICAL EXAMINER'S LABORATORY
MADRAS

The Determination of Small Amounts of Boron by means of Quinalizarin

BY G. STANLEY SMITH, B.Sc., A.I.C.

THE intensely coloured solutions of many hydroxyanthraquinones in concentrated sulphuric acid show, on the addition of boric acid, a marked change of colour that can be used for their identification. The colour-change has also been used by Feigl[1] for the microchemical detection of boric acid, quinalizarin furnishing the most sensitive test.

Feigl's procedure is as follows:—Evaporate to dryness one drop of the weakly alkaline solution in a micro-crucible, add 2 to 3 drops of a 0·01 per cent. solution of quinalizarin in concentrated sulphuric acid and warm gently. In the presence of boric acid the violet solution becomes blue. The method is sensitive to 0·06γ of boron. It is spoilt by fluorides and also by nitrates, ferricyanides and other oxidising agents, but the latter may be prevented by previous ignition from interfering. Metallic salts lower the sensitivity only slightly.

A test that has to be conducted in a medium of concentrated sulphuric acid has not such general applicability as one that can be made in more dilute acid. During an investigation into the colour changes in various concentrations of sulphuric acid it was found that the most sensitive change occurred in about 92 to 94 per cent. by weight of H_2SO_4, and that the colour of the solution might be made the basis of a quantitative determination of boric acid. The change in this and slightly lower concentrations is from reddish-violet or pink to blue and, consequently, is more easily detected than a change from bluish-violet to blue.

Boric acid produces a change of colour in all concentrations of sulphuric acid down to about 44 per cent. by weight. The sensitivity at first increases as the sulphuric acid concentration is lowered until about 93 per cent. is attained and then decreases. Under 85 per cent. the decrease is rapid and the sensitivity in the lower concentrations is very poor.

The minimum amount that can be detected appears to be about 0·012γ of boric acid or 0·002γ of boron, one drop each (0·02 ml.) of very dilute solutions of boric acid and quinalizarin in 93 per cent. sulphuric acid being used.

On the gradual addition of water to a solution of quinalizarin in concentrated sulphuric acid the bluish-violet colour changes progressively through various shades of reddish-violet and red to orange. The presence of boric acid counteracts to some extent the colour change produced by water; thus, a solution of quinalizarin in 87·5 per cent. sulphuric acid matches one in 69 per cent. sulphuric acid containing 0·01 g. of boric acid per 10 ml. In concentrations below 78 per cent. an excess of boric acid fails to give a blue colour.

TABLE I

COLOUR CHANGES IN VARIOUS CONCENTRATIONS OF SULPHURIC ACID

Volume of solution, 10 ml.; quinalizarin, 0·25 mg.

Sulphuric acid, per cent., by weight	Colour	Addition of 0·01 g. boric acid
99·5 to 97·5	Bluish-violet	Blue
94	Reddish-violet	Blue
88 to 80	Red	Blue
78	Red	Bluish-violet
73 to 69	Red	Red (slight violet tinge)
55	Orange	Pink
44	Pinkish-yellow	Orange

TABLE II

SENSITIVITY IN VARIOUS CONCENTRATIONS OF SULPHURIC ACID

Volume of solution, 10 ml.; quinalizarin, 0·05 mg.

Sulphuric acid, per cent., by weight	Minimum quantity in mg. of boric acid to give	
	definite change	blue colour
99·5	about 0·01	about 0·03
97·5	„ 0·005	„ 0·03
94 to 92	„ 0·001	„ 0·04
87·5	„ 0·005	„ 0·25
78	„ 0·2	„ 20

The rapidity of the colour-change increases as the sulphuric acid concentration decreases, unless a large excess of boric acid is added. In concentrated sulphuric acid a permanent colour, bluish-violet or blue, is obtained only after several hours; in 92 to 94 per cent. five minutes is sufficient; and in 87·5 per cent. the change is practically immediate.

The colours, when fully developed, are stable almost indefinitely, if the solutions are kept in closed tubes to avoid absorption of water.

The effect of heat is to develop a pink shade, which tends to mask the effect due to boric acid.

The colour appears to be specific for boric acid in the absence of such substances as nitrates and dichromates, fluorides, and those that give very noticeable colours in sulphuric acid. None of the common metals spoils the test, so that it is quite suitable for the detection of boron in alloys and minerals. The sample may be attacked by sodium hydroxide, by fusion with alkali carbonate or disodium phosphate and metaphosphoric acid, followed by careful solution in sulphuric acid, or by direct solution in sulphuric acid under a reflux condenser. Also, the test may be applied to a distillate obtained by the usual method, since methyl alcohol may partly or wholly replace the water in the test solution.

The method employed in estimating boric acid consists in comparing the colour of a solution obtained from the material or solution under examination with the colours of other solutions containing known amounts of boric acid, the sulphuric acid and quinalizarin concentrations being the same in all. When large proportions of other elements are present, the solutions compared should contain approximately the same amounts of these elements. The chief advantage of using somewhat diluted sulphuric acid is that the necessity for making the solution under examination alkaline and evaporating it to dryness is avoided.

The method has been applied particularly to the determination of boron in aluminium-silicon alloys.

The behaviour of the solutions in 93 per cent. sulphuric acid towards petroleum spirit is interesting. On shaking the reddish-violet and blue solutions with A.R. petroleum spirit, 40/60°, the colours appear to be practically unchanged, but if petroleum spirit, 100/120° is used, the reddish-violet boric acid-free solution turns a blood-red colour and the blue solution containing boric acid turns yellowish-green. The petroleum spirit layers remain colourless. This effect has been obtained with petroleum spirit from various sources.

METHOD.—Suitable concentrations of sulphuric acid for the colorimetric determination of boric acid are obtained by diluting 9 and 4 volumes, respectively, of the concentrated acid with 1 volume of water. The colour-change in the latter concentration permits of the determination of about 5 or 6 times the amount of boric acid that can be determined in the former concentration, but the sensitivity is lowered proportionally.

The sulphuric acid should be A.R. or Analar grade, 97·5 to 99·5 per cent. by weight. It should be free from nitrates, and 0·0005 per cent. solutions of quinalizarin in the diluted acids should have stable pink colours, though of different shades.

Determination of 0·001 *mg. to* 0·040 *mg. of boric acid.*—Standard solutions:—Boric acid, 0·0050 g. per l. of H_2SO_4(9 : 1); quinalizarin, 0·01 g. per 100 ml. of H_2SO_4(9 : 1).

Transfer, by means of a pipette, 1 ml. of the aqueous solution to be tested to a small comparison tube or test-tube, add 9 ml. of concentrated sulphuric acid from a burette, mix and cool the solution. In another tube place the same volume of 9 : 1 sulphuric acid and add to each 0·5 ml. of the quinalizarin solution. Mix the solution well and compare the colours. If a reddish-violet, bluish-violet or blue colour forms within five minutes and if interfering substances are absent, boric acid is present. A pure blue colour implies the presence of at least 0·04 mg. of boric acid in the quantity of material tested.

Assuming that a reddish-violet or bluish-violet colour is produced, it may be matched with standards. In several similar tubes place different volumes of the standard boric acid solution, at most 8 ml., and make up each to the same volume as the test solution with H_2SO_4 (9 : 1). Add to each 0·5 ml. of the quinalizarin solution, mix and leave for 5 minutes. One of these may be slightly bluer and one slightly pinker than the test solution. Further standards should now be prepared and an exact match obtained.

The method is accurate to a millionth of a gram of boric acid over the range 1 to 40γ, provided that the sulphuric acid concentrations in all the solutions are approximately the same. This condition is realisable in practice, since an error of as much as 5 per cent. in measuring the water for any one test causes the formation of a colour corresponding with that given by a decrease of the boric acid content to an extent just observable, that is to say, of about 1γ. When standardised apparatus, pipettes and burettes for small volumes, and measuring cylinders for the stock solutions are used and all the solutions are made up from the same batch of sulphuric acid, the concentrations of the solutions used for matching are sufficiently close.

If less than 1γ boric acid is indicated, the original solution may be concentrated somewhat, after being made alkaline, and the test applied to the stronger solution.

Quantities of 0·005 mg. to 0·25 mg. of boric acid.—Standard solutions:—Boric acid, 0·0250 g. per l. of H_2SO_4 (4 : 1); quinalizarin, 0·01 g. per 100 ml. of H_2SO_4 (4 : 1).

Mix 2 ml. of the aqueous solution to be tested with 8 ml. of concentrated sulphuric acid, add 0·5 ml. of the quinalizarin solution, and proceed as before, using 4 : 1 in place of 9 : 1 acid. The accuracy is about 5γ over the range 5 to 250γ.

BORON IN ALUMINIUM-SILICON ALLOYS.—Boron is not a common constituent of aluminium-silicon alloys, but its occasional use as a modifying agent and the requirements of specifications, such as B.S.S., L. 33, necessitate an accurate method for the determination of small quantities of this element. Existing methods, with the possible exception of spectrographic methods, are tedious or untrustworthy. It is doubtful whether all the boron can be distilled as methyl borate in the presence of large quantities of aluminium salts and silica, and the removal of the aluminium before the distillation by means of ammonia is unsatisfactory, since it does not serve as a separation from borates; moreover, it is almost impossible to filter the solution, unless the silica has been removed by methods necessarily causing loss of boric acid by volatilisation and leaving some of the boron associated with the silica.

If the possible boron-content of the material is disregarded, an error may be caused in the silicon determination by reason of the volatility of boron fluoride.

By proceeding as in Callendar's method for silicon[8] a clear solution may be obtained, suitable for the determination of boron by means of quinalizarin. Dissolve the sample and a boron-free alloy in separate crucibles as follows:

Treat 0·5 g. of the fine drillings with 20 ml. of 10 per cent. sodium hydroxide solution in a large nickel crucible fitted with a lid. After the initial attack is over wash down the lid and sides, evaporate the solution nearly to dryness on the hot-plate, add about 20 ml. of water, boil for a short time, and pour the solution into 30 ml. of 60 per cent. sulphuric acid. Wash out the crucible with a little acid and then several times with water, removing any solid particles. Make up the solution to 100 ml. with water.

Place 1 ml. of each of the solutions so obtained in small comparison tubes, add 8 ml. of concentrated sulphuric acid, mix and cool the solutions, and add 0·5 ml. of 0·01 per cent. quinalizarin solution. Compare the colours after 5 minutes and determine any boron present by the method given above, except that 1 ml. of the solution of the boron-free alloy should be added to each standard that is made up.

The method is suitable for quantities of boron down to 0·01 per cent. of the alloy.

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The Application of Controlled Potential to Microchemical Electrolytic Analysis

BY A. J. LINDSEY, M.SC., A.I.C., AND H. J. S. SAND, D.SC., PH.D., F.I.C.

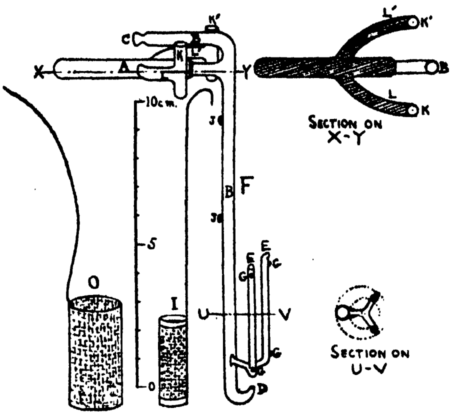
(*Read at the Meeting on November* 6, 1935)

THE electrolytic method has been applied by Pregl[1] with considerable success in gravimetric microchemical analysis. Pregl describes the determination of copper, and the method has since been tested[2,3,5,10] and extended to silver,[7] cadmium,[7] mercury,[7,8] lead,[12] nickel,[4,10] and cobalt.[4]

Microchemical electrolytic methods should lend themselves particularly well to separations in which the potential difference between the anode and cathode is controlled without the use of an auxiliary electrode. Hitherto, however, no work appears to have been done in this direction. The relatively small currents employed even in determinations requiring no more than ten to fifteen minutes make it possible to keep the potential difference due to ohmic resistance in the electrolyte small, provided that a relatively large anode surrounding the cathode is employed. By this means, too, and by the use of suitable depolarisers, it should be possible to maintain the variation of the anode potential within narrow limits.

The electrodes described by Pregl, which consist of a cylindrical gauze cathode with a central wire anode are excellent for the condition prescribed by him of a boiling electrolyte, the stream of steam bubbles rising from the anode causing vigorous circulation and freeing the electrolyte from dissolved oxygen. For the purpose under review they are, however, unsuitable. The use of depolarisers, which we recommend, makes boiling temperature unnecessary, and, to compensate for the absence of this, stirring is effected by means of bubbles of an indifferent gas.

FIGURE 1



The assembly of the frame and the electrodes we have designed is explained by Figs. 1 and 2. Vertical and square-on horizontal dimensions are shown to scale. The inner or working electrode I (Fig. 1) is the ordinary Pregl cathode with the beads removed. The outer electrode, the body of which is made entirely of thin gauze, is explained fully by O (Fig. 1). F is the frame on which the electrodes are placed. It will be seen that it is built upon the inlet tube, B, of the gas used for stirring. The entrance, C, is opened to a nipple, the outlet, D, being turned up into a capillary jet. Near the top of B is sealed a glass rod, A, which is held by the boss-head, G, on the small stand shown in Fig. 2. The rod, A, carries two arms, L and L', to which mercury cups, K and K', are attached. The arrangement of A, L, L', K and K' is shown to scale in plan on a level with the position in the view. Near the bottom of B the 2-mm. rods, E, are fitted to form a cage into which the working electrode, I, can be dropped, so as to sit securely, electrical connection being made by means of the mercury cup, K'. The outer electrode is held permanently in position by the beads, G, sealed on to the rods E, as shown in the figure, the connecting wire being twisted round the beads, J, and dipped into the mercury cup, K. The cups, K and K', are permanently connected by platinum-tipped wires to the terminals T and T' fitted to the stand (Fig. 2). Horizontal dimensions may be taken from the sectional plan U–V. The electrolysis vessel is a test-tube ("Monax") of internal diameter 2 cm., cut to a length of about 10 cm., and holding about 12 ml. to the top of the electrodes. It rests on the bottom of a 100-ml. beaker, which serves as a water-bath, and it is held securely in position by the frame, F. The ring, R, which supports a gauze, and to which the micro-burner, M, is also attached, is so constructed that it may be swung aside.

Method of Working.—The electrodes having been put in position, the solution is placed in the test-tube, which is raised from below until the frame touches the bottom. The water-bath is likewise raised from below, and the ring, R, swung into position. Water is then added until the electrodes are covered, and the gas used for stirring is admitted, its flow being adjusted by means of a screw clip near the apparatus. The gas is taken from a hydrogen, nitrogen, or carbon dioxide cylinder, as the case may be, and in order that no inconvenient pressure may arise, it passes through a T-tube, the open end of which dips into a boiling-tube containing a suitable amount of water. The water-bath is raised to the required temperature, the current is switched on, and the voltage between the electrodes is raised from zero to the correct value by moving the slider, S (Fig. 5). This value is maintained until the metal is exhausted, the current usually falling to about one-tenth of its original value. The test-tube is then washed down with a fine jet of water, and the residual current is maintained for a few minutes. The water-bath is now removed and replaced by a beaker of cold water, current and stirring gas being left on. When the electrolyte is at room temperature, first the water-bath and then the test-tube is lowered, while the exposed parts of the inner electrode are sprayed by a jet of water until the whole has been washed. The inner electrode is then removed by a platinum hook, dipped rapidly in turn into water, alcohol and ether, and dried by holding it in the hot air above a bunsen flame for a few minutes, or preferably in the dryer (Fig. 3). The end which has dipped into the mercury contact cup is then heated to redness to remove traces of mercury which may adhere to the wire (see also Okáč[4]). The electrode is allowed to cool for about a minute in the air, and is then transferred to the micro-balance, and, after the lapse of fifteen minutes,

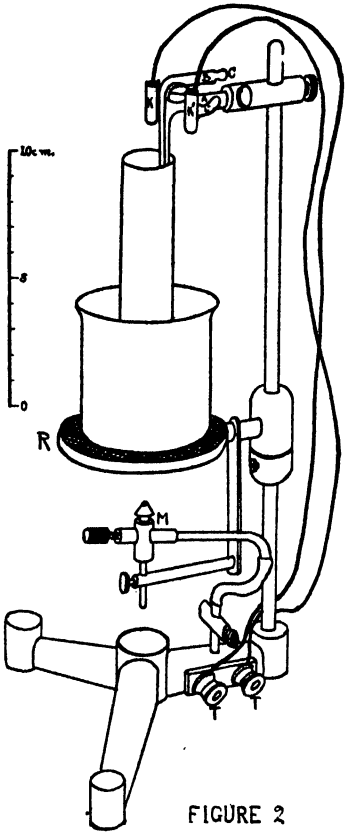


FIGURE 2

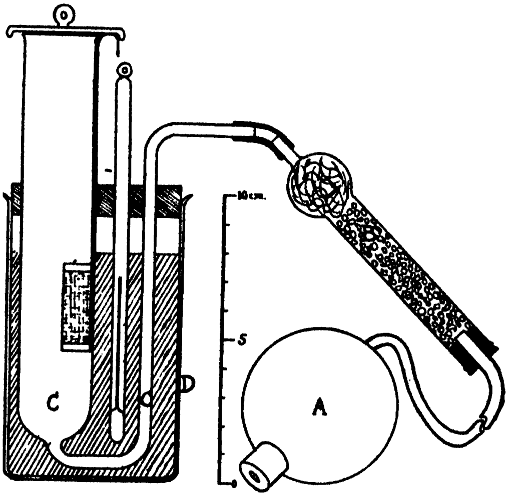


FIGURE 3

weighed. During this time the side doors of the balance case are kept open, whilst the large outer case in which the balance is mounted is closed. A counterpoise for the electrode is used. A convenient tool, shown in Fig. 4, for carrying the electrode and placing it across the hooks of the (Bunge) microchemical balance without handling was devised. The technique of transferring the electrode from the platinum hook to the silver-plated tool is readily acquired.

The drying apparatus, to which reference was made above, is shown to scale in Fig. 3. In this a stream of air from the hand-bellows, A, is blown through the tube, B, which is filled with calcium chloride and cotton wool, and then through the glass U-tube, C, which is heated to over 100° C. in a bath, D, of boiling water and glycerin. The electrode is hung in the wide limb, as shown, while the stream of warm dry air is passed over it. One minute is sufficient to dry most deposits to constant weight. When not in use the tube is conveniently kept covered by means of a crucible lid.

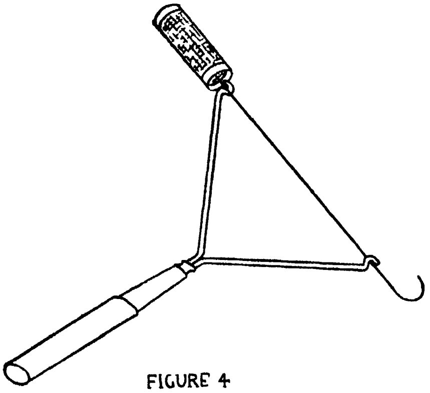


FIGURE 4

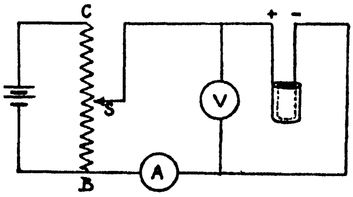


FIGURE 5

The electrical circuit employed is shown in Fig. 5. It will be seen that current from two accumulators is passed through the rheostat, BC, the voltage required being tapped off between B and the slider, S. The voltmeter, V, was a high-resistance instrument (50,000 ohms). If a low resistance instrument is employed, allowance may possibly have to be made for the current flowing through it.

Since depolarisers are employed during the application of the method described, we have thought it useful to make a study of the anodic depolarisation produced by the sulphates and hydrochlorides of hydrazine and hydroxylamine under varying conditions of current and temperature. We have also examined the effect of the addition of salts of copper and silver to the acid electrolyte. We have found that hydrazine salts appear to be efficient under all conditions; the depolarising efficiency of hydroxylamine is appreciably smaller, but is improved by the presence of chloride and of copper ions. Figs. 6*a* and 6*b* show the results we have obtained. Currents of varying strength were passed between the electrodes described by us,[13] the electrolyte consisting of 80 ml. of a 2·5 per cent. solution of copper sulphate crystals to which 5 ml. of 2 *N* sulphuric acid and 5 ml. of depolariser solution were added. According to the experiment the depolariser contained 2 per cent. of either the sulphate or the hydrochloride of hydrazine or hydroxylamine. The outer electrode was made the anode and the potential difference between it and a saturated calomel electrode with sodium sulphate as connecting liquid was measured as described by us.[14] Logarithms of the current density are plotted as abscissae, and the potential differences between the anode and the auxiliary electrode as ordinates. The actual values of the current density have also been entered. The latter have been arrived at by dividing currents by the overall single surface area of the electrode employed. It will be seen from Fig. 6*a*, by comparing the no-depolariser line with that obtained with hydrazine sulphate, that the latter reduces the polarisation at ordinary temperature by about 1·3 volt. The depolarising efficiency of hydrazine hydrochloride is slightly smaller than that of the sulphate. The depolarising efficiency of hydroxylamine salts is smaller and, in the absence of copper ions, smaller still. In all cases, as shown by Fig. 6*b*, rise of temperature increases depolarising efficiency, this being particularly marked for hydroxylamine salts at low current density.

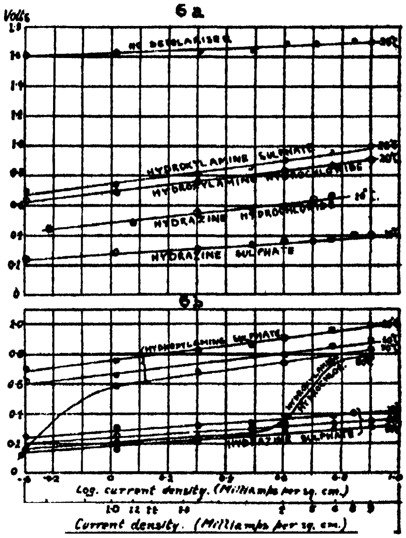


FIGURE 6

The micro-method described may be employed for copper depositions and other determinations to which the Pregl method is applicable, even when boiling temperature is not maintained. In addition, it has been applied successfully to the separation of bismuth from lead and that of copper from tin and other metals in chloride solutions, which processes cannot be carried out with Pregl's electrodes and without the control of cathode potential. These methods will be described later.

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The Micro-Electrolytic Determination of Bismuth and Lead and their Separation by Graded Potential

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(*Read at the Meeting, November* 6, 1935)

No methods for the quantitative micro-electrolytic deposition of bismuth or for its separation from lead have yet been described. The present investigation has resulted in a satisfactory technique for the separation and determination of both metals. Brantner and Hecht[1] did not recommend the micro-electrolytic deposition of lead as dioxide, but it should be noted that they used a platinum micro-crucible as the anode and were not able to control the conditions sufficiently well to ensure reproducible results. The electrolysis apparatus of Pregl may be used for the determination of lead as dioxide at the boiling-point of the solution, and the results are in agreement with those obtained by the technique later to be described. The determination of bismuth alone and its separation from lead cannot be effected with Pregl's electrodes.

The anodic deposition of lead from a nitric acid solution as dioxide in the presence of bismuth always results in the occlusion of bismuth in the deposit. Previous work upon the separation has been carried out on a macro-scale by Sand,[2] Lassieur[3] and Collin.[4] In each case a reducing agent was added to the solution to prevent the anodic deposition of lead, and the cathodic deposition of bismuth was controlled by the method of graded potential. As reducing agent Sand used glucose or tartaric acid, Lassieur hydroxylamine, and Collin hydrazine; but whereas the two former authors subsequently deposited the lead as metal, the last destroyed the hydrazine and deposited the lead as dioxide. This method has been modified to suit the micro-apparatus described in the previous paper, and the general method outlined therein has been followed.

THE DETERMINATION OF BISMUTH.—To the bismuth solution, containing up to 6 mg. of bismuth, 1 ml. of nitric acid (sp.gr. 1·42), two drops of hydrazine hydrate solution (50 per cent.), and sufficient water to make a volume of 12 ml. are added. The solution is heated to 60 to 70° C. in the water-bath of the apparatus previously described (p. 740), and electrolysed at an anode-to-cathode potential of 0·8 volt. The current falls during the electrolysis from about 80 milliamperes to about 10 milliamperes. Nitrogen stirring is employed. After 10 minutes the tube is washed down with a fine jet of water, and the potential across the cell is increased to 0·9 volt. After a further 3 minutes the tube is cooled by replacing the hot water-bath by a cold bath, and the electrolysis is terminated by rapidly replacing the tube by a shorter tube containing distilled water. The electrode is dipped successively into alcohol and ether and transferred to the dryer for one minute. The deposit and cathode are weighed as described previously. The following analytical results were obtained using the above method.

Bismuth taken, 5·595 mg.
Bismuth found, 5·62, 5·60, 5·60 and 5·62 mg.

The deposit was in each case dark grey and firmly adherent to the cathode. The deposits were removed by solution in nitric acid.

THE DETERMINATION OF LEAD.—To the lead solution, containing up to 6 mg. of lead, are added 2 ml. of nitric acid (sp.gr. 1·42), and the whole is diluted to about 12 ml. in the apparatus previously described, the previously weighed inner electrode being made the anode. The solution is heated almost to boiling by means of the micro-burner, and is kept at this temperature during the whole time of electrolysis. Stirring is effected by means of a nitrogen stream. The anode-to-cathode potential necessary is 1·0 volt, and the current passing is from 120 to 200 milliamperes. The potential is not critical, and higher values may be used if necessary to maintain the current density. After 7 minutes the sides of the tube are washed down with a jet of water, and in another 3 minutes the electrolysis is terminated by rapidly replacing the tube by a shorter one containing distilled water. The electrode is then dipped in turn into alcohol and ether and transferred to the dryer for one minute. The deposit and cathode are re-weighed as before described. Determinations of lead made according to the above procedure are slightly high. This is in harmony with the findings of previous workers,[5,6,7,8,9] and from the results a factor appropriate to the method was calculated. No lead could be detected in the residual liquid after making it alkaline with ammonia and then adding hydrogen sulphide.

The following results were obtained by the above method:

Lead taken mg.	Lead dioxide found mg.	Lead found mg.
4·068	4·76	4·09
	4·71	4·05
	4·74	4·08
	4·73	4·07
	4·72	4·06
	4·73	4·07
Mean	4·73	

From the mean of the six determinations of the dioxide the factor 0·860 was calculated, from which the values of column three were obtained.

THE SEPARATION OF BISMUTH AND LEAD.—To the solution containing not more than 6 mg. of each metal, are added 1 ml. of nitric acid (sp.gr. 1·42) and two drops of hydrazine hydrate solution (50 per cent.). The volume is made up to 12 or 13 ml., and the solution is electrolysed at 60 to 70° C., with nitrogen stirring. The anode-cathode potential is kept at 0·8 volt, and the current density falls during the electrolysis from an initial value of about 70 milliamperes to about 10 milliamperes. After 10 minutes from the start the tube is washed down, and the electrolysis is continued at an anode-cathode potential of 0·9 volt for another 2 minutes, when the hot water-bath is replaced by a cold one. With the current still on, the test-tube is rapidly replaced by a shorter one containing about 12 or 14 ml. of distilled water. The cathode is then removed, and after being dipped into alcohol and ether is dried as usual.

The deposit and cathode are weighed as previously described.

The solution from which the bismuth has been removed is transferred to a 50-ml. tall-form beaker, some of the water which has been used for washing the electrodes being used to effect complete transference. Fifty per cent. sodium hydroxide solution is added, drop by drop, until the precipitate redissolves, after which a few (10 to 20) mg. of sodium peroxide are added, and the beaker is heated (with a cover) until no more oxygen evolution is apparent. The whole is neutralised with concentrated nitric acid, and an excess of 4 ml. of acid is added. Finally, the remainder of the washing-water is transferred. With care the volume may be kept as low as 30 or 35 ml. The solution is electrolysed in the beaker at a temperature just below boiling-point, with nitrogen-stirring and an anode-cathode potential of 1·2 volt. This value is not critical, and a higher potential may be used. The current may be as great as 300 milliamperes. No water-bath is used, the beaker being heated directly by means of the micro-burner. After 12 minutes the beaker is washed down, and in a further 3 minutes deposition is complete. If, however, the electrode is weighed, the result is always found to be very high, owing, no doubt, to sodium salts occluded by the dioxide. Accordingly an electrolysis test-tube containing 2 ml. of nitric acid and 12 ml. of water is placed in the position occupied by the beaker, and the current is reversed to redissolve the dioxide. When the centre electrode is free from deposit the current is reversed again, and the lead deposited as described earlier. The following results were obtained by this method:

Metal taken		Found		
Bismuth mg.	Lead mg.	Bismuth mg.	Lead dioxide mg.	Lead mg.
1·11	4·11	1·09	4·77	4·10
2·22	4·11	2·26	4·78	4·11
3·36	4·11	3·36	4·83	4·15
5·65	4·11	5·62	4·77	4·10
5·65	4·11	5·62	4·75	4·09

The values recorded in the last column were calculated from the weights of lead dioxide found, by means of the factor (0·860) determined earlier.

I wish to express my thanks to Dr. H. J. S. Sand for his suggestions and continued interest in this work.

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Notes

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A NOTE ON THE ANALYSIS OF IODINE OINTMENTS

We have recently examined several samples of iodine ointment, the genuineness of which was in question, and the resulting cases were reported among the Legal Notes (ANALYST, 1935, **60**, 245). Since then we have received a number of queries as to the methods of analysis we adopted. It would, therefore, appear that a brief résumé of these methods might be of value, particularly in view of the fact that we ourselves met with some difficulty in finding satisfactory methods from the literature on the subject.

There are two main varieties of iodine ointment—the ordinary and the stainless. For the former the 1914 B.P. required iodine 4 per cent., potassium iodide 4 per cent., glycerin 12 per cent., and prepared lard 80 per cent.—a formula modified in the B.P.C. 1934 by replacing the base of glycerin and prepared lard by simple ointment, in order to avoid the combination of the iodine with the fatty base discussed later. For the stainless ointment the B.P.C. 1934 requires iodine 5 per cent., arachis oil 15 per cent. and yellow soft paraffin 80 per cent. In addition, there are several similar proprietary ointments, the main feature of which is that the iodine is in organic combination with a fatty base. The iodine-content of these is often declared on the label.

The methods described by Evers and Elsdon (ANALYST, 1922, **47**, 197) for determining the free iodine and potassium iodide in the B.P. ointment are not adequate, as they do not take into consideration the iodine in organic combination. Pullen (*Pharm. J.*, 1922, **35**, 610) has shown that in an ointment prepared according to the B.P. formula combination occurs between the free iodine and the lard, the uncombined iodine being reduced by a third in several months, although the total quantity remains practically unchanged. Fried (*Yearbook of Pharmacy*, 1915, 270) and Warren (*ibid.*, 1918, 334) have shown that equilibrium between the free and combined iodine in the ointment is attained after about 30 per cent. of the free iodine has been absorbed, and that the presence of potassium iodide is essential to limit this change. In justice to the manufacturer, it is necessary to ascertain the total iodine actually used in compounding, which will naturally include both the free halogen and that which has subsequently combined with the base.

The free iodine and the potassium iodide are readily determined by the methods of Evers and Elsdon (*loc. cit.*). For the determination of the total iodine the method of Thompson and Snyder (*Yearbook of Pharmacy*, 1917, 102), which consists in saponification of the ointment with alcoholic potash, removal of the unsaponifiable matter, and subsequent liberation of the iodine with hydrogen peroxide in acid solution, was found to be unsatisfactory; in fact, the authors themselves admit that alcoholic potash does not take up the iodine absorbed by the ointment base. Nor was alkaline fusion (Middleton, *Quart. J. Pharm.*, 1929, **12**, 536), which gives excellent results with biological materials like thyroid gland (ANALYST, 1932, **57**, 603), found to be entirely satisfactory when applied to these ointments. The following method was finally adopted and gave very consistent results:

About 2 g. of the well-mixed ointment are weighed in an open capsule, which may be prepared by cutting the bottom off a test-tube, a little powdered pumice is added, and the whole is dropped into 100 ml. of strong sulphuric acid in a 400-ml. distilling flask connected with an air-condenser fitted with a bulb-tube dipping under 50 ml. of water in a tall cylinder. The distillation is then begun, heat being applied slowly at first. The distillate consists mainly of hydriodic and sulphurous acids. The contents of the flask are kept gently boiling for 3 to 4 hours, at the end of which time the whole of the iodine will have distilled. The condenser and delivery tube are rinsed through with cold water, and the distillate and washings are filtered to remove the small quantity of organic matter (fatty acids) which generally distils. Excess of nitric acid, followed by silver nitrate solution, is added, the mixture is heated to boiling, and the precipitate of silver iodide is collected in an alundum crucible,* washed, dried and weighed.

Since stainless iodine ointment contains neither free iodine nor potassium iodide, the methods of Evers and Elsdon† are not applicable to such preparations. The total iodine may, however, be determined by the method just described.

The ordinary and the stainless iodine ointments examined by us have contained one or more of the following substances in addition to iodine and, in most instances, potassium iodide:—paraffinum molle, arachis oil, lard, oleic acid, glycerin and parogen, the last being compounded from liquid paraffin, oleic acid, ammoniated alcohol and 90 per cent. alcohol.

In no case was any difficulty encountered. It is, however, possible that volatile iodine compounds, such as iodoform, would distil over partly unchanged, or even completely so. Other methods of dealing with such compounds must, therefore, be employed, and, in any case, ointments containing them do not comply with any formula for *iodine* ointment in the B.P. or the B.P.C. The purpose of the present note is merely to give a method of dealing with such preparations as may contain fatty or other substances capable of absorbing iodine.

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THE EXAMINATION OF RUBBED SPEARMINT

Spearmint (*Mentha viridis*) which has been dried and rubbed through sieves, is sold in considerable quantities in packet form for culinary use. The detection, in 1933, of the adulteration of foreign spearmint with the dried leaves of *Ailanthus glandulosa*[1] has resulted in increased attention being paid to the examination of dried spearmint. Stress has been laid upon the necessity of microscopic examination, and tentative limits have been suggested for ash and essential oil content.[2]

Some time ago we had occasion to examine a consignment of dried spearmint which had been rejected by another analyst. The mint was said to contain a small quantity of *Ailanthus*. Upon microscopic examination about 1 per cent. of striated cuticle, reminiscent of *Ailanthus* was found. This striated epidermis occurred only in very small fragments, and careful examination failed to reveal any of the characteristic hairs of *Ailanthus* or any calcium oxalate crystals. Moreover, when the specimens were compared under the microscope with *Ailanthus*, it was seen that there were differences in structure, although the resemblance was close.

In view of the facts that the spearmint in question was grown in Bedfordshire, the farm being open to inspection, and that no *Ailanthus* trees were in the vicinity, it was concluded that some unidentified weed had contaminated the consignment. It was decided to investigate the matter further, and to this end some of the growing mint was plucked and dried in air in the laboratory, and the leaves were rubbed through a sieve. The rubbed leaves were prepared for examination by boiling for two minutes with 1 per cent. caustic potash, centrifuging and washing with water, followed by treatment with chloral hydrate solution. Finally, the leaves were washed in water and mounted in dilute glycerin. Upon microscopical examination the same striated epidermis was found to be present in an amount not exceeding 1 per cent. Further examination of the mint leaves showed that the striated cuticle came from an area at the base of the midrib.

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* In the gravimetric determination of halides we have found alundum crucibles much more satisfactory than the ordinary Gooch type.

† Evers and Elsdon (*Analysis of Drugs and Chemicals*, 1929, p. 259) state that the stainless ointment should contain not more than 0·5 per cent. of free iodine when determined by their method.

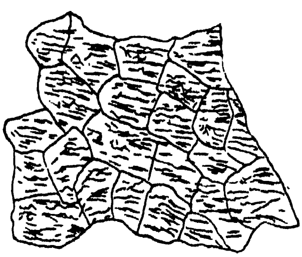
Fig. 1

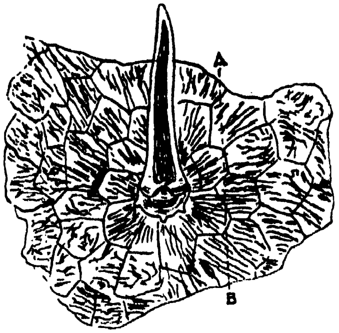

Fig. 2

A drawing (Fig. 1) of the structure was made with a Watson–Abbe eyepiece, and a drawing of the upper epidermis of *Ailanthus* is shown in Fig. 2. If a line be drawn from A to B on the *Ailanthus* picture (Fig. 2) and the area to the right compared with a similar area on Fig. 1, it will be seen that there is some similarity in the structure of the cells. During subsequent work on this subject it was found that the palisade ratio, suggested by Zörnig and Weiss,[3] and developed by Wallis and Dewar,[4] afforded another means for distinguishing *Ailanthus*.

In our experiments we found the palisade number for spearmint to be 5–7, whilst that of *Ailanthus* was 7–13. Measurement of the length of the stomata showed an upper limit of 30μ with an average of 24μ for spearmint, whilst *Ailanthus* stomata often reach 50μ.

It therefore follows that perfectly genuine spearmint may show a small proportion of striated epidermis somewhat resembling that of *Ailanthus*, but the presence of the latter should not be reported unless other diagnostic features are also present.

Our thanks are due to Mr. T. E. Wallis for helpful advice and to the directors of Messrs. Potter & Clarke, Ltd., for permission to publish this note.

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DETERMINATION OF THE CALCIUM AND PHOSPHATE CONTENT OF BONES

WITHIN the past two years a number of analyses of bones were made for the University of Pennsylvania Museum. These bones were specimens taken from excavations in Egypt, Central America and Alaska. Results and conclusions of this work, together with the work of other investigators, will be published later. This note presents a comparison of the results obtained by several analytical methods which were used in the analysis of standard solutions and bone solutions.

The chemical analysis of each sample of bone required the percentage of carbonate, calcium and phosphate. The carbonate-content was determined in the usual way by decomposing an air-dried sample of bone with hydrochloric acid. The carbon dioxide was absorbed in a Midvale absorption tube containing ascarite. The solution containing the calcium chloride and phosphoric acid was transferred from the digestion flask to a 500-ml. measuring flask and diluted to a known volume. Aliquot portions were used for the determinations.

A standard solution was prepared by dissolving a known amount of pure acid potassium phosphate, calcium carbonate and a trace of magnesium oxide in a small amount of hydrochloric acid and diluting to the mark in a 500-ml. measuring flask. This gave a solution similar in composition to that of the dissolved bones. Aliquot parts of this solution were used to test the methods.

DETERMINATION OF CALCIUM.—The commonly used basic acetate procedure[1] was tried and found to be unsatisfactory with only one precipitation. In order to obtain good results two precipitations were necessary. The most satisfactory method, alike for speed and accuracy, is that given by Hillebrand and Lundell.[2] The calcium is precipitated in the presence of the phosphate with an excess of oxalic acid and ammonium oxalate and filtered on to a Gooch crucible. The Gooch crucible containing the precipitate is transferred to a beaker and treated with sulphuric acid, and the liberated oxalic acid is titrated with standard potassium permanganate solution.

TABLE I

CALCIUM DETERMINATIONS

A. Standard Solution. B. Bone Solutions.

Percentage calcium (one precipitation)

	Basic acetate method	Oxalic acid and ammonium oxalate method	Calculated value
A.	19·54	20·15	20·17
	19·43	20·15	
B.	31·92	33·74	
	25·26	25·58	
	31·06	31·11	
	26·55	26·92	
	30·11	30·42	
	30·74	31·36	

Another standard solution containing 6·5 per cent. of magnesium was used to determine the accuracy of the oxalic acid and ammonium oxalate method. With one precipitation, in the presence of the higher percentage of magnesium, two determinations gave 18·87 and 18·86 per cent. of calcium. The calculated value was 18·63 per cent.

DETERMINATION OF PHOSPHORUS.—The phosphate was precipitated with an excess of ammonium molybdate.[3] The phosphomolybdate was dissolved in an excess of standard (carbonate-free) sodium hydroxide solution. The excess of base was titrated with standard hydrochloric acid, phenolphthalein being used as indicator. Standardisations and titrations for each method were carried out under the same conditions. Results obtained from titration of the phosphomolybdate in the hot (80° C.), and in the cold (room temperature) are given in Table II.

TABLE II

PHOSPHATE DETERMINATIONS

A. Standard Solution. B. Bone Solutions.

Percentage of phosphate (PO_4).

	Hot titration	Cold titration	Calculated
A.	34·18	34·07	
	33·70	33·66	
	34·26	33·12	
	33·11	33·66	
	33·89	33·13	
Average	33·83	33·53	33·56
B.	43·29	42·12	
	35·16	34·96	
	35·87	34·10	
	44·50	43·50	
	42·55	42·06	
	39·72	38·30	

SUMMARY.—1. During an investigation of the chemical composition of specimen bones taken from recent excavations, it was necessary to check the accuracy of the volumetric methods used in the determination of calcium and phosphorus.

2. The basic acetate method for the determination of calcium in the presence of phosphorus was compared with the oxalic acid and ammonium oxalate method. With one precipitation the latter method gave excellent results for calcium, whereas the basic acetate method gave low results. In the presence of 6·5 per cent. of magnesium the oxalic acid and ammonium oxalate method gave high results, but these were within the limit of error for this type of work.

3. The precipitation of phosphorus as ammonium phosphomolybdate and titration with standard alkali gave high results when the titration was carried out in a hot solution. The end-point was more distinct in titrations made at room temperature.

The authors gratefully acknowledge a grant from the Faculty Research Committee of the University.

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DETECTION OF FORMALDEHYDE IN MILK

In testing for the presence of formaldehyde in milk by Hehner's method, trouble has occasionally been experienced, owing to the composition of present-day commercial sulphuric acid. This is probably due to the presence of sulphur dioxide, and, possibly, also of other impurities, introduced in the contact process, which were absent from acid obtained by the lead chamber process. It appears preferable, therefore, to use pure acid with the addition of a trace of a ferric salt and to carry out a control test with every delivery of acid. Acid which gives negative colour reactions may frequently be sensitised by the addition of a trace of potassium permanganate, but the sensitivity thus obtained is usually of a temporary nature only, and it is better, therefore, to discard such deliveries for use in this reaction.

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A SOUND-PROOF BOX FOR ELECTRICALLY-DRIVEN LABORATORY CENTRIFUGES

Owing to the rapid development of colorimetric and micro-methods of chemical analysis, many laboratories are now adopting methods in which centrifugal separations play an important part. The advantages of an electrically-driven centrifuge are obvious, but many have one very characteristic disadvantage, namely, they are noisy.

The noise set up by the concurrent use of two electrically-driven blood centrifuges standing[*] on a teak bench in these laboratories was of a high-pitched and piercing nature, and an attempt was made to find a method of eliminating this disturbance. Several of the simpler specifics were tried, including the mounting of the machine upon rubber and typewriter mats, soft asbestos and cotton-wool pads, but none of these proved very satisfactory. It was decided, therefore, that a sound-proof box would offer the only satisfactory remedy, and the writer's model, described below, was found to be almost sound-proof.

Construction of the Box.—A box just large enough[†] to accommodate the centrifuge was constructed of ¾" deal boards. It was fitted with a lift-up lid, secured by hinges at the back and fastened by a bolt at the front. When open, the lid rested against the laboratory wall, but, where this is impracticable, a stay-hinge could be fitted.

The inside surfaces of the box were covered with rubber sponge mats,[‡] faced on one side only with a thin solid layer of rubber. They were fixed by means of nails, so that the sponge surface was in contact with the wood. The bottom was completely covered with a 1" thick mat, but, for all other surfaces, mats of ½" thickness were used. The side mats were cut so as to stand upon the bottom mat and to reach to within about ¼ inch of the top of the box, thus allowing the covered lid to close down tightly wood to wood, with its attached sponge mat (cut to the internal dimensions of the box) fitting snugly inside on to the tops of the side mats. The four corners were also plugged with 1" × 1" strips of the material, extending from the bottom mat to within about ¼ inch of the top of the box. A small hole was cut at the top of one side to allow the flex to pass through to the external electrical resistance. The centrifuge was lowered into the box and allowed to rest upon the bottom mat. The machine must not be screwed down, nor must the metal safety bowl and lid be omitted. It will be noticed that the revolution counter cannot be used with the machine enclosed in the box, but the resistance slide may be easily calibrated occasionally to serve as a rough guide to the speed of the centrifuge.

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[*] They were not screwed down, as in this and many laboratories portability is an important factor.

[†] The internal dimensions of the box were about 16" × 16" × 15" high, in order to accommodate a machine 12½" high by 12½" diameter.

[‡] Supplied, specially cut to size, by Messrs. Hellewell & Co., Liverpool.

The act of opening or closing the box in addition to the removal or replacement of the metal cover, as the case may be, may seem to be a rather tiresome procedure, but actually the habit becomes almost effortless after a short time. The portability of the equipment is in no way impaired if the electrical resistance is not fixed to the box, and the centrifuge can be moved in or out at will.

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

METROPOLITAN BOROUGH OF FULHAM

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1934

CHOCOLATE EASTER EGGS.—Four samples of chocolate Easter eggs were condemned on account of the presence of maize starch, two samples containing 10 per cent., and the other two 20 per cent. of this ingredient. The vendors claimed that the eggs were not labelled as chocolate, but such an explanation is of little value, since chocolate eggs were demanded, and there is no doubt that this type of product is sold to an unsuspecting public in the hope that it will be bought as chocolate.

COPPER IN TOMATO PURÉE.—Four samples of tomato purée were reported as adulterated on account of the presence of copper. Two samples contained 12 parts per million, whilst the other two contained 20 parts of copper, and 87 and 345 parts, respectively, of tin. These purées were all of Continental origin.

COMPOUND TINCTURE OF CARDAMOMS.—Three samples were found to be of B.P. 1914 quality, instead of conforming to the present Pharmacopoeia. The present preparation contains 60 per cent. of alcohol, as compared with 45 per cent. in the 1914 B.P., and, consequently, a larger proportion of active ingredients.

GREY POWDER CONTAINING TALC.—Two samples of grey powder were adulterated. One of these was deficient to the extent of 50 per cent. of mercury, and was compounded with talc instead of chalk; the other was 92 per cent. deficient in mercury.

THYROID TABLETS.—Four samples of thyroid tablets were submitted for examination. The samples were too small to permit of anything like a complete examination, but the quantities of iodine, calculated on the stated dose of thyroid present, which serve as a guide to the amounts of thyroxine, varied from 0·159 to 0·573 per cent. It was noted that only two of the samples were sold as being of pharmacopoeial quality, but it is unsafe to allow such a wide variation in the potency of active drugs. This variation can normally only be detected by the doctor through the effect he observes on the patient. It is to be hoped, therefore, that in future Pharmacopoeias it may be possible to give some other test which can be carried out on quantities which the normal purchaser would obtain.

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METROPOLITAN BOROUGH OF HAMMERSMITH

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1934

PLACE OF ABSTRACTION OF FAT FROM MILK.—In one prosecution the Bench took the unique course of dismissing a summons on the ground that, although they were satisfied that the abstraction of fat certified had indeed taken place, yet they were not satisfied as to *where* it had taken place. They expressed the hope that the Council would take the matter further in order to settle the point. So far as I am aware, there is no precedent for such action.

"REAL" CREAM CONFECTIONERY.—Seven samples, out of a total of 11, of various types of cream confectionery were reported as adulterated on account of the use of cream substitutes as a filling material. Proceedings were instituted in respect of four samples, and convictions were obtained in each case, the total penalties inflicted amounting to £12 2s. The use of such terms as "cream buns" or "cream sponge sandwich" is calculated to deceive the purchaser, and it is a very debatable point as to how far the word "cream" can legitimately be employed in the generic, instead of the specific sense. There is no doubt, however, that most purchasers of this confectionery buy it under the impression that the cream filling really is cream. In the cases cited above the articles were sold as "*real* cream" buns, cakes, etc.; hence, there could be no two views as to whether deception was intended or not.

IODINE OINTMENT.—Of six samples of iodine ointment analysed during the year, no less than 5 were condemned. Two were ointments of a very different type, made from methyl salicylate (oil of wintergreen) and petroleum jelly, with the addition of a dark brown colouring matter to make them resemble iodine ointment. In the remaining three instances traces only of iodine or potassium iodide were present, whereas the British Pharmacopoeia of 1914, and the British Pharmaceutical Codex of 1923 and 1934, require four per cent. of each.

F. W. EDWARDS

CITY AND COUNTY OF KINGSTON-UPON-HULL

ANNUAL REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR THE YEAR 1934

OF the total number of samples of food and drugs examined during the year, 1229 were official and 664 informal samples.

DIRT IN MILK.—During the year only 7 of 1112 samples of milk (0·6 per cent.) showed an appreciable amount of visible dirt in the ordinary one-third pint samples. This contrasts favourably with the condition in 1925, when 10·4 per cent. of the samples were dirty.

When one of these ordinary-sized samples is found to contain appreciable amounts of visible dirt (which is detected by allowing the milk to remain at rest for one–two hours in its original bottle in a sloping position, by which means the dirt is largely concentrated in a small area at the bottom of the bottle), the fact is reported to the Sampling Officers of the Health Department, and as soon as practicable a larger sample (3 pints, divided into three one-pint samples) is obtained with special precautions, when the amount and character of the dirt (if any) can be ascertained with some accuracy on the larger sample then available for analysis.

The Milk and Dairies Order, 1926, enjoins cleanliness on the cowkeeper, without giving the local authority any real means of determining whether the milk has been produced by such cowkeeper under the conditions laid down in the Order.

It is contended by the writer that milk which can be proved by analysis to be dirty (that is, to contain on examination by a standard method more than two parts of moist extraneous matters in 100,000 parts of the milk, such extraneous matters consisting partly or largely of *dung*) has certainly not been produced under the conditions laid down in the Order quoted, and that evidence that milk is so contaminated should be sufficient to obtain the conviction of the producer in the Courts. Many convictions have been obtained by the Corporation under the Sale of Food and Drugs Act, but a local authority would be in a much stronger position if a standard of chemical cleanliness were definitely laid down under the Milk and Dairies Order, 1926. An attempt was made to secure the inclusion of the desired clause in the Draft Order as first issued, but it was unsuccessful.

CREAM BISCUITS.—One of 7 samples of biscuits examined attracted special attention, since it was labelled "Dairy Cream Biscuits"—a description which it was thought entitled a purchaser to expect some proportion of real cream as an ingredient of these biscuits. About three-quarters of the weight of the biscuits was actual farinaceous material, with one-quarter as a "paste" consisting of three parts of sugar with one part of fat. The fat contained at least 95 per cent. of a vegetable fat of the nature of coconut fat, with not more than 5 per cent. of butter-fat. This analysis showed that the name applied to this product was unjustified, and the makers finally agreed to alter the name, omitting the offending word. Any regulations made by the Ministry of Health on standards and definitions for foods should include products such as these so-called "cream" biscuits.

POTTED MEATS.—Ten of 26 samples of potted meat were reported as adulterated. They contained, respectively, 3·5, 4·0, 7·5, 2·3, 4·8, and 5·7 per cent. of moist farinaceous material (mainly wheat flour); 5·2 per cent. excess water and 500 parts per million of boric acid; 5 per cent. excess water and 400 parts per million of boric acid; 3·0 and 6·2 per cent. excess water. The standards of composition adopted by the Corporation include a maximum of 70 per cent. of water, and freedom from foreign farinaceous ingredients.

SULPHUR GASES IN THE AIR.—The daily determinations of the total amount of sulphur gases in the air of the city have been continued throughout the year under review, and the following are the results obtained. These figures for sulphur gases follow those for total pollution in the central area, and show a diminution compared with the previous year.

SULPHUR ACIDS IN THE AIR (CITY OF HULL)
(in terms of sulphur dioxide, volumes per million)

1934 Month	Daily maximum	Daily minimum	Daily average
January	0·237	0·025	0·108
February	0·234	0·050	0·110
March	0·200	0·027	0·079
April	0·113	0·027	0·069
May	0·077	0·019	0·045
June	0·092	0·016	0·043
July	0·053	0·010	0·025
August	0·059	0·013	0·028
September	0·065	0·012	0·031
October	0·117	0·027	0·065
November	0·224	0·050	0·118
December	0·142	0·022	0·068

A. R. TANKARD

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

CHOCOLATE ROLL DEFICIENT IN CHOCOLATE

On August 17th, at Aylesbury Petty Sessions, a London wholesale firm of bakers and confectioners was summoned for wilfully giving, with an article of food, namely, a chocolate Swiss roll, a label which falsely described the article sold, and also with giving a false warranty contrary to Section 30 of the Food and Drugs (Adulteration) Act, 1928. Mr. C. B. Guthrie, barrister, instructed by the solicitors of the London Master Bakers' and Confectioners' Protection Society, pleaded not guilty to both charges.

Outlining the case for the prosecution, Mr. S. E. Wilkins stated that an Inspector of the county purchased a chocolate roll for analysis, and, in consequence of the report received, the Inspector, at a later date, took a further sample on delivery at the retailer's premises. The report from the Public Analyst was as follows:—"The sample is not genuine, being artificially coloured to resemble chocolate." Under the heading of observations it stated, "The amount of chocolate present, if any, is negligible, being less than one per cent."

The roll purchased was in a cardboard carton marked " . . . finest quality Swiss Roll. Is made of the finest quality flour." At each end was marked, " . . . 6d. Swiss Roll chocolate." The roll inside was wrapped in grease-proof paper marked, " . . . chocolate roll—purity guaranteed. Made from the finest quality ingredients; made in a model bakery under ideal conditions. 6d."

Mr. Wilkins informed the Bench that there was no standard fixed for chocolate roll or cake, but there was ample authority that, if there be no standard, the justices must fix one on the evidence. There need not necessarily be a quantitative standard, but there might be a minimum standard.

When the rolls were delivered to the retailer an invoice was handed to him showing them to be "balance of order," and at the bottom of that invoice was a guarantee as follows:—"We guarantee all foods supplied by us to be of the nature, substance and quality described, and to comply with the provisions of the Sale of Food and Drugs Act, 1928, and with all other statutory requirements or regulations relating to the sale of food."

Mr. Eric Voelcker, F.I.C., one of the Public Analysts for Buckinghamshire, referred to analysing the samples and to issuing the certificates. In cross-examination the witness suggested that not less than 4 per cent. of dry fat-free cocoa material should be used to give the proper flavour and taste and to justify the description "chocolate." In reply to Mr. Wilkins, witness said that the sample did not taste of cocoa at all. The colouring matter should not take the place of the ingredient which was necessary. It should be chocolate in nature and not in colour.

Mr. T. Macara, F.I.C., supported the views of the previous witness, and said that if an article was described as "Chocolate Swiss Roll," there should be sufficient cocoa powder to give it both the colour and flavour of chocolate. From his own observations he would say that about 4 per cent. of non-fatty cocoa material was required to give a chocolate flavour. An article with less than 1 per cent. would not have the flavour or colour of chocolate.

Mr. Guthrie submitted that in law both summonses must fail. Dealing with the alleged false warranty, he submitted that there must be a warranty in writing delivered when the contract of sale had been completed, and the warranty relied [illegible] the goods when delivered, and was not a warranty within the meaning of the section of the Act under which these proceedings had been taken. The goods must be sold with the warranty, but the retailer had had the contract of sale some days before the goods had been delivered. The invoice was not a contract of sale. With regard to the other summons, Mr. Guthrie referred to Section 18 of the Act, and submitted that the officials of the county had failed to comply with the procedure of the Act. In reply, Mr. Wilkins submitted that the warranty was in order and that the purchase was not completed until the delivery of the goods. Regarding the other summons, he stated that they were not dealing with Section 18, but with Section 16 of the Act, which provided that a sample may be taken at the time of delivery.

There was considerable discussion of the points raised, and, after a short retirement, the Bench upheld the objection of the defence regarding the false warranty, but were of the opinion that the prosecution were acting, in the other summons, under Section 16 of the Act, and, therefore, complied with the law.

In submitting the case for the defence, Mr. Guthrie said that these rolls did not purport to be chocolate cake—they were not sold as such. Nobody buying them expected chocolate cake, but merely rolls with a chocolate flavour. The word "chocolate" was used to differentiate these rolls from those of other flavours.

The managing director of the firm said that they used 1·03 per cent. of cocoa powder, and had used this amount since 1926. Approximately 16,000 chocolate rolls were made each week, and no complaint had ever been received from the public.

Evidence was also given by the president and a past-president of the London Master Bakers' and Confectioners' Protection Society that the amount of cocoa powder used was a reasonable proportion, although, personally they used a little more.

The Chairman announced that, in respect of the dismissed summons, costs of three guineas would be allowed to defendants. In respect of the summons for a false description they had decided to convict. Evidence for the defence showed that something like 2 or 3 per cent. of cocoa powder was a reasonable amount to use. They would inflict a penalty of £3 and costs amounting to £14 5s.

Department of Scientific and Industrial Research

Food Investigation

THE REFRIGERATED GAS-STORAGE OF APPLES*

THIS leaflet deals with the process in which control of the composition of the atmosphere in the store is the principal feature. The outstanding advantage of gas-storage is that ripening of the fruit is slowed down to about half the rate in air at the same temperature. Carbon dioxide has the specific effect of retarding the change of the green colour of the fruit to yellow, and also preserves the hardness of the fruit almost unchanged. The surface-eating Tortrix larvae are quickly killed in gas-storage.

Directions are given for the pre-treatment of fruit before storage, for the interval to be allowed between gathering and storage, and for the time for unloading the store.

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* Leaflet No. 6. By F. Kidd, M.A., D.Sc., and C. West, M.A., D.Sc. Obtainable gratis on application to the Secretary, Department of Scientific and Industrial Research, 16, Old Queen Street, Westminster, S.W.1.

There are also sections dealing with the size of the chamber, the methods of making the chamber gas-tight, and of obtaining the correct atmosphere in the store. In this connection it is pointed out that the rate at which carbon dioxide is produced is dependent upon the temperature; for instance, apples produce approximately twice as much carbon dioxide at 60° F. as at 40° F. Control of carbon dioxide and of oxygen by restricted and regulated ventilation alone will provide the required atmosphere only when the concentrations of the two gases add up to 21 per cent. Chemical absorption of the oxygen can be controlled, either by regulated circulation of the atmosphere of the chamber over a large quantity of absorbent, or by introducing limited charges of the absorbent into the chamber at intervals as required.

The following table gives the temperatures and atmospheres recommended for the storage of home-grown apples.*

Variety	Temperature† °F.	Carbon dioxide Per Cent.	Oxygen Per Cent.
Culinary Varieties—			
Annie Elizabeth ..	34 to 35	0	21 (air)
Bramley's Seedling ..	40	8 to 10	13 to 11‡
King Edward VII ..	37 to 40	5 to 10	2·5
Lane's Prince Albert..	39 to 40	5	2·5 to 5
Lord Derby	40	8 to 10	13 to 11‡
Monarch	34	5	2·5 to 5
Newton Wonder ..	34	0	21 (air)
Stirling Castle ..	40	8 to 10	13 to 11‡
Dessert Varieties—			
Blenheim Orange ..	37 to 38	0	21 (air)
Cox's Orange Pippin	39 to 40	5	2·5
Ellison's Orange ..	34	5	2·5 to 5
King Pippin	39 to 40	0	21 (air)
Laxton's Superb ..	40	10	2·5
Worcester Pearmain	34 to 35	5	2·5 to 5

The humidity of the atmosphere in gas-stores for apples has so far presented no difficulty in practice. Under commercial conditions it varies between 85 and 98 per cent. of saturation. The relative humidity of the atmosphere actually surrounding the fruit is the main factor determining the rate at which it loses water.

There is now much evidence that the accumulation of volatile substances produced by the fruit is harmful, and may cause superficial scald. It has been found in practice that when ripening fruit is placed in gas-storage with unripe, green fruit, damage is caused to the latter, even when oiled wrappers are used.

The capacity of the refrigerating plant should be sufficient to reduce the temperature of the fruit from 65° F. to 40° F., with an external temperature of 70° F., within 4 to 5 days after the chamber is closed.

The leaflet concludes with a description of the most suitable boxes for fruit and of methods of stacking in the store, and of the thermometers and instruments used for indicating the composition of the atmosphere. There is also a list of scientific references and an appendix on the cost of gas-storage.

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* It should be noted that a few varieties keep best in ordinary cold storage. Amongst these are the two varieties that are particularly susceptible to superficial scald, *viz.* Newton Wonder and Annie Elizabeth.

† Temperature of flesh of apple.

‡ Atmospheres obtainable by controlled ventilation, as practised in commercial gas-storage.

Government of Madras

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1934

In his annual report Dr. Clive Newcomb states that 1553 cases were investigated during the year, as compared with 1518 in 1933. The total number of human poisoning cases was 327, poison being detected in 174. Oleander heads the list of poisons with 41 cases, opium or its alkaloids come next with 24 cases, closely followed by datura or mydriatic alkaloids with 23 cases. Several of the cases present points of analytical interest.

MERCURIC CHLORIDE POISONING.—In one case a man was given poisoned milk and died four days later. In the vomit 25 grains of corrosive sublimate were found, but the visceral matter contained only traces of mercury. In another case (suicide), in which a man confessed to having swallowed mercuric chloride in coffee, death occurred about a fortnight later; only extremely minute quantities of mercury were present in the viscera. On the other hand, in two cases in which death was very rapid large quantities of mercury (30 and 50 grains) were found in the viscera. Thus, in fatal cases of mercuric chloride poisoning, if the victim lives for some time after taking the poison, only very small amounts of mercury may be found in the viscera.

Analytical Notes on the Determination of Mercury in Viscera.—(*Cf.* p. 734.)

MADAR JUICE POISONING.—There were two cases of death from drinking madar juice. From the viscera in each case extracts giving the reactions described in my Annual Report for 1933 (ANALYST, 1934, **59**, 542) were obtained.

Ester Test for Madar Juice.—The sulphuric acid method of esterification of madar juice often yields a liquid the odour of which is masked to a large extent by the odour of sulphur dioxide, ether, etc. We found that the ester test for madar juice could be more conveniently made in the following manner:—The material, rendered slightly alkaline and dried, is extracted with alcohol, and the solution is esterified by passing dry hydrogen chloride gas through the alcoholic solution. Then a solution of potassium hydroxide is added to neutralise the hydrochloric acid while the contents are kept cool. If madar juice was present in the original material, the liquid now exhibits a pleasant odour strongly resembling that of fresh ripe strawberries. This test can be carried out even with small quantities in a test-tube. If desired, the neutralised solution can be distilled to obtain the ester or esters.

OLEANDER POISONING.—Thirty-six of the 41 cases in which oleander was detected were fatal. The symptoms of oleander poisoning, so far as can be gathered from the histories furnished, appear to be tingling of tongue, shivering of hands and feet, and, later, of the body, epigastric pain, vomiting, in a few cases purging, rapidity and failure of pulse, and asphyxial symptoms. In some cases convulsions also occurred. Unconsciousness set in only towards the end.

The post-mortem examination showed that in about half of the fatal cases the heart was contracted and all its chambers empty. In about a third of the cases the right side of the heart was filled with dark blood and the left side of the heart was empty. In practically all the cases the lungs were congested. There was also congestion of liver, spleen, kidneys, and brain in most of the cases, and the stomach and intestines showed patches of congestion.

The cases were mostly suicidal, and it seems as if oleander were taking the place of opium as the poison of choice for suicide.

GLORIOSA SUPERBA POISONING.—A man of 45 committed suicide by eating the root of *Gloriosa superba*. From the viscera a poisonous extract similar to that from the root was obtained. It was found that neither the acid nor the alkaline ethereal extract obtained in the extraction of the root by the Stas-Otto process was fatal to frogs, but, on adding ether to an alcoholic (rectified spirit) extract, a whitish precipitate was obtained, which, when separated and injected into frogs, killed them. The precipitate was freely soluble in water, but insoluble in absolute alcohol, ether, chloroform or amyl alcohol. Yellow oleander seeds, when treated in the same manner, yielded a similar poisonous precipitate which, however, was soluble in absolute alcohol as well as in amyl alcohol. Further, the precipitate from yellow oleander seeds yielded a blue colour on boiling with dilute hydrochloric acid (*cf.* Annual Report for 1932). The precipitate from *Gloriosa superba* did not give any colour with hydrochloric acid. Moreover, yellow oleander seeds in addition yield an acid ether extract poisonous to frogs and giving a purple colour with concentrated sulphuric acid. The poisonous extract from *Gloriosa superba*, obtained as described above, appears to be a glucoside. Its further nature is under investigation.

The microscopic examination of *Gloriosa superba* root revealed: (1) An epidermal tissue of elongated cells containing minute, perfectly spherical bodies, all nearly of the same size, about three to four $m\mu$ in diameter, many of them having crenated edges and radiating striæ. These curious bodies are not destroyed by boiling the tissue in water, in chloral hydrate solution, or in hydrochloric acid, but appear to be soluble in potassium hydroxide solution; (2) a parenchymatous tissue of thin-walled polygonal cells closely packed with starch granules. The starch granules consist mostly of ovoid grains, with some spherical, semi-spherical and semi-elliptical grains. There is a well-marked hilum in each granule, and there are distinct concentric striations. The hilum is situated at the *broader* end of the ovoid granules at a distance of about a third of its diameter. The average diameter of most of the grains is about $35m\mu$. There are, however, a few grains with diameters of $15m\mu$, and some with diameters of $45m\mu$. In some of the spherical grains the hilum is in the centre of the grain. The starch grains of *Gloriosa superba* differ from those of potato starch in the fact that in potato we find much larger grains (70 to $110m\mu$ in diameter), and the hilum in potato starch is found close to the *narrow* end of the grain. Spiral vessels and bast fibres are rather scarce.

CANNABIS INDICA POISONING.—A father was suspected of having poisoned his son. There were no definite post-mortem signs, as the body was decomposed. The suspected poison—a powder—was also sent. The suspected poison was found to be the powdered leaf of Indian hemp, and we obtained from the stomach a poisonous extract which gave a positive Beam's test with alcoholic hydrochloric acid. The other Beam's test, *viz.* the formation of a purple colour on addition of alcoholic potash to a petroleum spirit extract of the substance and evaporation at room temperature, was negative, and this test does not work satisfactorily in our hands, even with some known specimens of Indian hemp leaf. We were, however, not absolutely certain of the presence of Indian hemp, as we could not get any sediment resembling Indian hemp under the microscope. There have been fatal cases of poisoning by Indian hemp, both accidental and suicidal, and cases have also been reported where the drug appears to have been used for the purpose of facilitating the commission of an offence, but this is the first fatal homicidal case we have met.

KARU VEERATHALAI LEAVES (*Elaeodendron glaucum*, Pers.).—We examined last year a case of poisoning caused by drinking a decoction of the leaves of this plant. The symptoms were not stated. At the post-mortem examination the heart cavities were found to be empty. The lungs were soft and slate coloured; the stomach and intestines were congested with a thick yellow liquid in the latter, and the membranes of the brain were vascular. We obtained from the stomach a poisonous resin similar to the poisonous extract obtained from the leaves and bark of *Elaeodendron glaucum*. This plant is a shrub occurring in the hotter parts of India. In *Watt's Dictionary of the Economic Products of India* it is stated that the root is a "specific" against snake bite (whether internally or externally is not stated). The bark is said to be used in native medicine and to be a virulent poison, and the leaves to be used as a fumigant to rouse women from hysterical fits. The leaves and bark were examined in this laboratory, and both yielded a poisonous resin which gave, in chloroformic solution, with acetic anhydride and sulphuric acid a green colour (Liebermann reaction). The resin was found to be freely soluble in chloroform and sparingly soluble in ether and in petroleum spirit.

JAMMI LEAVES (*Prosopis spicigera* L.).—Samples of leaves received were said to have been used in a suspected poisoning case, but we did not detect poison in the viscera. The leaves examined here gave a poisonous acid ethereal extract which did not give the Liebermann reaction for resin. It gave a brown colour when dissolved in acetic acid containing ferric sulphate, and floated on sulphuric acid containing a trace of iron (Keller's reaction). The extract did not reduce Fehling's solution.

PICROTOXIN POISONING.— A woman was found at bed-time to be suffering from pain in the stomach, with vomiting and convulsions. She died at about 4 a.m. the next day. The viscera were sent to us, but we had no information as to the nature of the poison swallowed. We obtained from the viscera an acid ethereal extract which (1) was crystalline, (2) reduced Fehling's solution, (3) killed a frog with convulsions, (4) gave a brick-red colour on treatment with potassium nitrate and concentrated sulphuric acid followed by solid potassium hydroxide, and (5) gave a bright red colour on treatment with a solution of benzaldehyde in absolute alcohol followed by the addition of concentrated sulphuric acid. We did not obtain any alkaloid from the viscera. We therefore concluded that the acid ethereal extract we had obtained was picrotoxin, the active principle of *Cocculus indicus*.

ACONITINE POISONING.—Three children were given a decoction of some root with castor oil. They became restless and developed tingling of the lips and tongue, burning sensation in the stomach, with numbness in the body and inability to walk. Two of them died. From the stomach of one of the victims we obtained aconitine, but could not find any in the stomach of the other. There is little doubt that both died of aconite poisoning. Our inability to find it is noteworthy as showing how difficult it may be to find it in the stomach, even when the patient has been poisoned by it.

IDENTIFICATION OF GUNPOWDER CARBON IN THE TISSUES.—A man was alleged to have been shot with a gun. There was an injury in the neck which might have been due to a gun-shot wound. The gun, we were told, was loaded with country gunpowder and pebbles, no leaden bullet or shot having been used. The tissues around the wound were sent to us for examination to ascertain whether the wound was caused by gun-shot. As an examination of the tissues for lead would have been of no use in this case, we digested portions of the tissues (1) in cold nitric acid and (2) in cold hydrochloric acid plus potassium chlorate. After the tissues had dissolved, a fine black deposit of carbon was seen at the bottom in each case, showing that carbon had been embedded in the tissues. Sections of the tissue examined under the microscope also showed black foreign particles. The detection of elementary carbon imbedded in the tissues of the wound suggested that the tissues had been subjected to the explosion of a black powder at close range.

IDENTIFICATION OF TYPEWRITERS.—Several cases requiring the identification of the machine on which a document had been typed were investigated, and the method outlined in my previous reports (ANALYST, **1934, 59,** 39, 544) was used with conclusive results.

Medical Research Council

(Privy Council)

THE DETERMINATION OF IODINE IN BIOLOGICAL SUBSTANCES*

THE work described in this Report was undertaken because it appeared that the methods commonly in use for the determination of minute amounts of iodine in the presence of organic matter were unsatisfactory. Stress is laid upon the point that precautions must be taken to ensure that the atmosphere of the laboratory cannot become contaminated from outside sources (*e.g.* by the use of iodine in an adjoining room). Failure to obtain low and constant "blanks" is a sure indication of adventitious contamination.

From a study of the colorimetric and volumetric processes, the conclusion is drawn that the personal error in matching colour is undoubtedly greater than in judging the end-point of titration in the volumetric process. On the other hand, with the volumetric method, it must be fully appreciated that the figure obtained by titration measures the oxidising power of the solution. In the presence of oxidising agents other than iodic acid (chlorine, bromine, bromate, iron, vanadium, etc.), the figure obtained is not a true measure of the iodine originally present. Furthermore, in the presence of certain substances (nitrite, bromide, organic matter), the iodic acid may be partly reduced, when the results will be low. In spite of these defects, however, experience has shown that, when due regard is paid to its limitations, the volumetric process is to be preferred as a standardised method, owing to its comparative freedom from personal error.

The titrations are carried out with $N/500$ thiosulphate solution, a micro-pipette or burette being used. Soluble arrowroot starch has been found to be the most suitable indicator. For the oxidation of the iodide to iodate bromine water is preferable to chlorine water, and the conditions under which hydriodic acid is quantitatively oxidised by bromine have been thoroughly examined. A carefully standardised method has been based on the results of the study of the various processes, including the extraction of the iodide, and the destruction of the organic matter under varying conditions.

Tables of results obtained by the standard method in experiments in which known quantities (in γ) were added to milk powder, milk, hay and blood, are given in full, and these are followed by a detailed description of the standard method, and of modifications thereof for use with milk, vegetable materials, and other materials (oils and fats, drinking water, waters containing nitrates, materials containing sulphates or other sulphur compounds, fish products, saline materials, and organic materials) containing relatively very little iodine.

There is a final section on precautions to be taken and sources of error, and the Report concludes with appendices on the preparation of soluble arrowroot starch and on the electrolytic preparation of iodine-free potassium hydroxide, and a bibliography of selected papers bearing on the subject.

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* Special Report, Series No. 201. By C. O. Harvey, B.Sc., A.I.C. Pp. 43. London: H.M. Stationery Office, Adastral House, Kingsway, W.C. August, 1935. Price 1s. net.

Ministry of Health

MILK PASTEURISING PLANTS

CIRCULAR 1473*

THE following circular has been issued to the Clerks of Local Authorities:

SIR,

1. I am directed by the Minister of Health to state, for the information of the Council, that he has recently published a Report by one of the Medical Officers of the Ministry on the Supervision of Milk Pasteurising Plants.†

2. The value of efficient pasteurisation in making milk safe for human consumption has become increasingly recognised during recent years, and was referred to with approval in the report of the Committee of the Economic Advisory Council on Cattle Diseases (Cmd. 4591); but if pasteurisation is to be effective in destroying the tubercle bacillus and other pathogenic organisms which may be present in milk, it is necessary that the process should be efficiently carried out.

3. At the present time, as the Council are aware, all milk sold under the designation "Pasteurised" is required to have been treated in the manner prescribed in Part IV of the Third Schedule to the Milk (Special Designations) Order, 1923, *i.e.* it must be retained at a temperature of not less than 145 degrees and not more than 150 degrees Fahrenheit for at least half an hour, and be immediately cooled to a temperature of not more than 55 degrees Fahrenheit. These requirements can be met with certainty only by what is known as "positive holding" (or the "holder method") by which the whole of the milk is retained or "held" at the required pasteurising temperature for the specified time.

4. There is evidence that some pasteurising plants at present in operation are imperfect in design or construction, or are not properly operated and controlled, with the result that efficient pasteurisation of the milk is not secured. The purpose of the present Report, as stated in the prefatory note, is to supply information on the subject of pasteurising plants, to explain the considerations involved in their construction, operation and cleaning, and to give some account of the appliances and methods employed in the subsidiary processes of bottle-washing and bottle-filling.

5. I am to remind the Council that one of the conditions subject to which licences for selling milk as "Pasteurised" may be granted is that the type of apparatus used for pasteurising and the methods employed shall be such as are satisfactory to the licensing authority. It is hoped that the Report will be of material assistance to officers of local authorities in reporting on applications for licences in respect of establishments at which the process of pasteurisation is proposed to be carried on, and in enabling those officers to exercise adequate supervision of pasteurising plants in respect of which a licence has been granted. With this end in view it is important that the Council should supply each of these officers with a copy of the Report.

6. A copy of this Circular is being sent to the Medical Officer of Health, and a copy of the Report is being sent to the Medical Officers of Health of those Authorities who are known to have issued licences in respect of pasteurising establishments. Further copies of the Circular and Report may be purchased through any bookseller or directly from His Majesty's Stationery Office.

I am, Sir,
Your obedient servant,
(*Signed*) A. K. MACLACHLAN
(Assistant Secretary)

May 16*th*, 1935.

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* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 1d. net.

† Report on the Supervision of Milk Pasteurising Plants by Sir Weldon Dalrymple-Champneys, Bt., M.A., D.M., F.R.C.P. (Public Health and Medical Subjects, No. 77, Price 1s. 3d.).

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Chlorine in the Fat of Flour. V. E. Munsey. (*J.A.O.A.C.*, 1935, **18**, 497–502.)—The bleaching of flour by a mixture of chlorine and nitrosyl chloride (Beta Chlora process), by chlorine alone, or by nitrogen trichloride (Agene process) increases the chlorine-content of the flour-fat. The Agene process adds only a small amount, but the Beta Chlora and chlorine processes add comparatively large quantities. The procedure recommended for determining the chlorine-content of the fat varies according as a green flame is or is not obtained when a little of the fat is heated on a copper wire. The most suitable solvent found for extracting the fat is aviation petrol, and the conversion of the chlorine in the extracted fat into the ionic form is effected by incineration.

For flour fats containing relatively little chlorine, the method given for the determination is virtually that described by Kent-Jones and Herd (Abst., ANALYST, 1930, **55**, 394), the result obtained being corrected by that of a blank determination with the reagents. For 28 unbleached flours examined in this way, the chlorine-content of the fat ranged from 0·4 to 1·8 p.p.m., the mean being 1·28. For unbleached rye flour the highest value found was 0·6, and the average 0·44 p.p.m. With Agene-bleached flours, the results varied from 2·5 to 13·7 p.p.m.

With flours bleached by the Beta Chlora or chlorine method, 75 g. of the flour are extracted with 150 ml. of aviation petrol, and the final determination of the chlorine may be carried out either gravimetrically as silver chloride or by the Volhard volumetric method. Details of the procedure are given. For 12 samples bleached by one of these two processes, chlorine-contents of 47·4 to 381 p.p.m. were found in the fats. T. H. P.

Transmission of Light through Eggshell. J. W. Givens, H. J. Almquist and E. L. R. Stokstad. (*Ind. Eng. Chem.*, 1935, **27**, 972–973.)—The visibility of the yolk-shadow in the commercial grading of eggs by "candling" will depend on any property of the shell which can control the passage of light through it. Tests were made on the transmission of light through eggshell in relation to thickness, water-content and protein-content. Water-content of the shell, determined by loss of weight when dried for 7 days *in vacuo* over phosphorus pentoxide at room temperature, was found to be the chief factor affecting light transmission, a sample with 1·8 per cent. of water giving a much higher transmission value than one with 0·9 per cent. The effect of water is probably due to the filling-in of the air-spaces between the calcite crystals in the shell with a medium of higher refractive index. Protein-content was found to be next in importance, the larger amounts of protein rendering the shell more opaque. Thickness of shell, and also the membranes present, had a minor effect on light-transmission. The two factors, *viz.* water and protein-content, are, as far as present knowledge indicates, independent of the true condition of eggs.

S. G. C.

Separation of Products resulting from the Enzymic Hydrolysis of Starch. J. L. Baker and H. F. E. Hulton. (*J. Inst. Brewing*, 1935, 41, 375–377.)—The use of alcohol for the separation of the conversion-products of starch is criticised. The bulk of the maltose, the principal sugar present, can easily be isolated and obtained in the crystalline state, but the non-crystallisable substances (*e.g.* dextrins) present difficulties, as maltose adheres to them mechanically and, according to some workers, even forms compounds of the malto-dextrin series (*cf.* Ling and Baker, *id.*, 1897, 287). The practice of designating a particular material in terms of its solubility, or otherwise, in alcohol of a particular strength is inaccurate, because the process of separation involves pouring gradually a syrupy solution of the material in water into alcohol of known strength. The concentration of the alcohol, therefore, decreases gradually during this operation, owing to the addition of water, so that (*e.g.*) a fraction said to be insoluble in 89·3 per cent. alcohol may really be a mixture of fractions insoluble in alcohol over a range of strengths which vary from 96 to 89·3 per cent. This criticism applies only to substances produced by the enzymic hydrolysis of starch by malt between room-temperature and 70° C. When barley diastase acts on starch paste the reaction is simple, about 60 per cent. of maltose and 40 per cent. of α-amylodextrin being formed (*cf.* Baker, *id.*, 1902, 628), which may be separated almost quantitatively by the conventional method, because the latter is insoluble in alcohol, so long as the strength is 80 per cent. or over. Numerous variations in the technique of the alcohol method and in the nature of the precipitating solvent have proved discouraging, but it is considered possible to eliminate the difficulty by adding rapidly to a certain volume of a solution of the conversion products in water, such a volume of 99 per cent. alcohol that the strength of the resulting alcohol of any desired value. In one experiment 800 ml. of 99 per cent. alcohol were added rapidly to 400 ml. of conversion products (containing 93 g. of total solids, and produced by the action of isolated malt diastase on potato starch paste for 1 hour at 130° F.). The mixture was shaken well, the final strength of the alcohol being 66 per cent. The $[\alpha]_{D3\cdot93}$ of the insoluble portion was 178·3 (original value, 152·3). The dextrin was dissolved in water, and alcohol was added so as to produce again an ultimate strength of 66 per cent., the $[\alpha]_{D3\cdot93}$ being then 185·5, and after a further similar treatment, 186·4. In this way it is possible in a relatively short time to obtain a dextrin similar in physical properties to the "stable dextrin" of Brown and Millar (*id.*, 1899, 461). J. G.

Comparison of Commercial Pectins. C. J. Van der Bie. (*Chem. Weekblad*, 1935, 32, 557–558.)—The following determinations were made on (*a*) a Californian citrus pectin; (*b*) and (*c*) two commercial citrus pectins from New York; (*d*) a German apple pectin; and (*e*) a slow-setting German pectin. *Methyl Alcohol.*—The material is saponified with warm alkali and acidified and distilled, the methyl alcohol in the distillate being oxidised to formaldehyde and determined colorimetrically with the Denigès fuchsin-sulphite reagent (*cf.* Von Fellenberg, *Biochem. Z.*, 1927, 85, 69). *Calcium Pectate.*—The material is saponified in the cold with sodium hydroxide solution, and the precipitate produced on addition of calcium chloride solution in the presence of acetic acid and heating is removed by filtration, washed, dried and weighed (*cf.* Mehlitz, *Koll. Z.*, 1927, **41**, 132). *Carbon Dioxide* is determined by heating the sample for 8 hours with 12 per cent. hydrochloric acid in a stream of air (free from carbon dioxide), the gas being absorbed in a known quantity of barium hydroxide solution, the excess of which is back-titrated with hydrochloric acid in the presence of an excess of barium chloride (*cf.* Baker, *infra*). *Setting-power.*—A mixture of 2 g. of the sample and 200 g. of sugar is added to a boiling mixture of 200 ml. of water and 20 ml. of 0·1 N tartaric acid in an aluminium pan, and the whole mixture is gently heated until the weight is 288 g., and allowed to set. The breaking-strength of the gel is determined by measuring, on a water-manometer, the pressure required to insert a plunger below the surface. Other determinations made were of ash, yield of furfural phloroglucide (Tollens), the relative viscosity at 27° C. of a 0·75 per cent. solution in water, the *p*H value (as determined by the Wulff strip method), and the acidity (titration of 10 ml. of a 0·75 per cent. solution with 1·075 N sodium hydroxide solution, phenolphthalein being used as indicator). The results are tabulated, the extreme values in each case being (in percentages), ash, 1·75 for (*e*) to 11·65 for (*a*); furfural phloroglucide, 19·5 to 37·05; methyl alcohol, 3·1 to 10·8; calcium pectate, 47·9 to 92·4; carbon dioxide, 10·90 to 19·0; viscosity, 1·71 to 3·82, although sample (*e*) gave the exceptionally high figure of 6·59 (see below); *p*H value, 2·8 to 4·2; acidity, 0·50 to 1·32 ml. The setting powers followed the decreasing order, (*a*), (*b*), (*e*), (*d*), and (*c*). The reasons for the slow-setting properties of (*e*) were investigated further, and the high viscosity was held to be responsible. However, (*e*) gave no colour with iodine and potassium iodide solution, and, although it contained more glucose than (*b*), addition of 0·5 per cent. of glucose to a solution of (*b*) raised the viscosity only from 3·73 to 3·83. According to the supplier, (*e*) was prepared by precipitation with aluminium salts and extraction with a solution of hydrochloric acid in alcohol; addition of 20 per cent. of aluminium nitrate to the solution of (*b*), however, changed the viscosity to 3·48, and produced a flocculent precipitate. Five g. of (*a*) were digested overnight with 100 ml. of 80 per cent. alcohol and 2 ml. of hydrochloric acid in the cold, and the residue was then removed from the extract (mainly calcium salts) by filtration and washed with the 80 per cent. alcohol until neutral, and then with absolute alcohol followed by dry ether; the ash-content fell to 3·35 per cent., and the 0·75 per cent. solution was less cloudy than originally and similar to that of (*e*), and had a viscosity of 6·62. The high viscosity of (*e*), therefore, appears to be due to the fact that the ash has been reduced by extraction with acid (*cf.* Baker and others, *Ind. Eng. Chem.*, 1926, **17**, 89; *Delaware Agr. Exp Stat. Bull.*, 1927, **149**; 1934, **187**; and following abstract). J. G.

Pectin in Hops. H. Fink and J. Hartmann. (*Woch. Brau.*, 1935, **52**, 221; *J. Inst. Brewing*, 1935, **41**, 380.)—Although the presence of pectin in hops has not hitherto been reported, it occurs in almost all non-woody vegetable tissues (*e.g.* roots, fruits and plant stems). It would remain undissolved by the solvents used to extract the bitter substances of hops, and might be overlooked in the extraction of hop tannins. For the detection of pectin (after F. Ehrlich) the material is digested with 10 to 15 times its weight of 1 per cent. sulphuric acid at a pressure of 4 atm. in order to produce galacturonic acid by hydrolysis, and this may be detected by known reactions. Pectins may then be determined by extracting the minced hops with alcohol and ether, 10 g. of the air-dry residue being boiled with 1 litre of 0·01 *N* citric acid under a reflux condenser for 24 hours. The liquid obtained after filtration is concentrated under reduced pressure to 250 ml., the calcium pectate in 40 ml. of this concentrate being determined by Mehlitz's method (*cf.* preceding abstract). Positive results with Ehrlich's test were obtained for hops, but not for ground barleys and malts, and 2 per cent. of pectin (calculated on the dry weight of the hops after extraction with alcohol and ether) was found by the quantitative method. It is considered that this quantity may be important from the brewing standpoint. J. G.

Constituents of the Wax-like Coating of the Pear, *Pyrus communis* L. K. S. Markley, S. B. Hendricks and C. E. Sando. (*J. Biol. Chem.*, 1935, **111**, 133–146.)—Peels obtained in the commercial canning of pears were extracted with ether and also with petroleum spirit. The ethereal extract, after further extraction with petroleum spirit, yielded ursolic acid. The extract obtained by petroleum spirit extraction contained about 40 per cent. of free and combined acids, approximately one-third of which were in the unesterified state. The solid acids, which comprised about one-eighth of the total acids, consisted of the usual mixed plant acids of the series C_{16} to C_{24}. The predominant acid was oleic, and only very small quantities of linolenic and linolic acids were isolated. No secondary alcohols or ketones were detected, but a small amount of glycerol was present, as well as the usual plant alcohols, which were at least ternary mixtures of the series C_{20} to C_{30}. The predominant hydrocarbon was *n*-nonacosane $C_{29}H_{60}$. The light green, low-melting pear wax, which was described by Seifert (*Landw. Versuchs.-Stat.*, 1895, **45**, 29), was, therefore, a complex mixture of free acids, esters, alcohols, and hydrocarbons, and his uncrystallisable *vitin-like* substance, which melted at 240° C., was impure ursolic acid. S. G. S.

Daturic Acid from the Seeds of *Datura stramonium*, Linn. B. L. Manjunath and S. Siddappa. (*J. Indian Chem. Soc.*, 1935, **12**, 400–404.)—Daturic acid, which has been regarded as equivalent to margaric acid, is the only acid with an uneven number of carbon atoms, the presence of which has hitherto been regarded as proved in an oil, but its presence in the oil from *Datura stramonium* seeds is not confirmed by the present work. The methyl esters of the solid fatty acids of the oil were repeatedly fractionated by the method of Francis, Piper and Malkin (*Proc. Roy. Soc.*, 1930, [A], **123**, 214), but no trace of daturic acid could be found. Palmitic, stearic and a small quantity of lignoceric acids only were present. A phytosterol of m.p. 134° C. was isolated from the unsaponifiable matter.

D. G. H.

Thiocyanogen Value of Indian Butter Fat (Ghee). U. D. Budhalakoti and K. C. Mukherji. (*J. Indian Chem. Soc.*, 1935, **12**, 455–458.)—Ten authenticated samples of butter or butter-fat from various parts of India were examined to find whether their linolic acid content, as estimated by determination of the thiocyanogen and iodine values, was sufficiently constant to be an index of purity. The percentage of linolic acid was found by multiplying the difference between the iodine value and thiocyanogen value by 1·104. The range of iodine values was wide (30 to 50), but that of the linolic acid content varied only from 3·5 to 5·4, so that this method appears equally applicable to Indian and Irish butters (*cf.* Arup, ANALYST, 1932, 57, 610). D. G. H.

Detection and Determination of 2:4-Dinitrophenol in Tablets and Capsules. I. S. Shupe. (*J.A.O.A.C.*, 1935, 18, 464–466.)—In the examination of these materials, which are used in the treatment of obesity, grinding and heating should be avoided, since otherwise explosion may occur. To detect 2:4-dinitrophenol, a sample is treated with water and 4 per cent. of sodium hydroxide, and the liquid filtered, if necessary. The filtrate is acidified with hydrochloric acid and extracted with chloroform. The extract is evaporated to small bulk on a water-bath, the last portions of the solvent being allowed to evaporate spontaneously. Part of the residue is treated with 2 ml. of 10 per cent. sulphuric acid and about 0·2 g. of powdered zinc and left for 10 minutes; appearance of a pink colour indicates nitrophenol. The liquid is then filtered, cooled, treated with 10 drops of 1 per cent. sodium nitrite solution, and, after remaining in the dark for 5 minutes, with 2 ml. of a saturated solution of β-naphthol in strong ammonia. After being left for 2 minutes, it is shaken with 10 ml. of ether, which assumes a pink or violet colour. From another portion of the residue from the chloroform extract, a 1 per cent. solution in 0·1 *N* sodium hydroxide is prepared and a drop of this treated, on a microscope slide, with a drop of 1 per cent. hydrochloric acid; microscopic examination shows characteristic rectangular, pale yellow crystals. The m.p. (114° C.) of the chloroform residue, recrystallised if necessary, and also the mixed m.p. with authentic 2 : 4-dinitrophenol, should also be determined.

To determine the dinitrophenol, a weighed quantity of the capsules (at least 20) is macerated with 20 ml. of 2 per cent. sodium hydroxide solution, which is transferred, with the aid of a little water, to a separating funnel, acidified with concentrated hydrochloric acid, and extracted with six successive portions of chloroform. The combined extracts are shaken with 20 ml. of 4 per cent. sodium hydroxide solution, and the lower layer is removed and repeatedly extracted with 20 ml. portions of the alkali until the yellow colour is eliminated. The alkaline solutions are mixed and made up to volume with water in a measuring flask. An aliquot part, containing about 0·1 g. of the dinitrophenol, is transferred to a glass-stoppered flask, diluted with water to 100 ml., neutralised with hydrochloric acid, and then made slightly alkaline with 4 per cent. sodium hydroxide solution. Twenty ml. of 0·1 *N* bromine solution are pipetted in, and 5 ml. of concentrated hydrochloric acid are added, and the stopper is at once inserted. The flask is shaken for a minute and cooled, 10 ml. of 15 per cent. potassium iodide are added, and the stoppered flask is thoroughly shaken. The stopper and neck of the flask are rinsed down, and the liquid is shaken with 1 ml. of chloroform, and titrated with 0·1 *N* sodium thiosulphate, with starch as indicator : 1 ml. of 0·1 *N* bromine ≡ 0·0092 g. of dinitrophenol ≡ 0·0103 g. of the anhydrous or 0·0112 g. of the monohydrated sodium derivative. T. H. P.

Determination of Hexamethylene-tetramine. R. Gros. (*J. Pharm. Chim.*, **1935, 127,** 241–244.)—Since hexamethylene-tetramine is hydrolysed by dilute sulphuric acid to formaldehyde and ammonia, the purity of a sample may be ascertained by determining the proportions of these products. To determine the formaldehyde, a 200-ml. refrigerating pipette connected with a 500 ml. Erlenmeyer flask is used (*cf.* Gros, *J. Pharm. Chim.*, 1934, **126**, 421). Eighteen ml. of Nessler's reagent (specially prepared a few hours before it is required by mixing 80 ml. of a solution of 13·55 g. of mercury chloride and 36 g. of potassium iodide in 250 ml. of water with 100 ml. of a solution containing 270 g. of sodium hydroxide per l. and filtering) and 2·5 ml. of a suspension of barium sulphate (10 per cent.) are introduced into the bulb of the apparatus, and, after a vacuum of 15 to 18 mm. of mercury has been obtained, 5 ml. of a 0·2 per cent. solution of hexamethylene-tetramine, about 10 ml. of distilled water, and 1 ml. of *N* sulphuric acid are added by means of the safety tap. After 10 minutes on the water-bath at 80° C., the refrigerator is brought into action, still with the mixture on the water-bath. Distillation is carried nearly to dryness, after which atmospheric pressure is restored in the apparatus, and without disconnection of the cold-water circulation, about 10 ml. of dilute hydrochloric acid (1 : 2) are introduced into the bulb (which is shaken), and then 20 ml. of a 0·05 *N* iodine solution are added. The water circulation is stopped, the rubber tubes are removed, and the bulb is separated from the flask, with shaking from time to time to assist solution of the reduced mercury. After 2 to 3 minutes the contents of the bulb are rinsed into a 500-ml. flask, and the excess of iodine left after complete solution of the mercury is titrated with a 0·05 *N* solution of sodium thiosulphate. The sample then contains $(20-n) \times 3{\cdot}5/6$ mg. of hexamethylene-tetramine, where n is the number of ml. required in the titration.

To determine the proportion of ammonia formed, 20 ml. of 0·02 *N* sulphuric acid are put into the refrigerating pipette, and into the Erlenmeyer flask (the walls of which have been washed to bring down the ammonium sulphate previously formed) are introduced 2 drops of phenolphthalein solution. After the necessary adaptations to the apparatus have been made and the vacuum established, baryta water is slowly introduced by means of the safety-tube until the mixture is alkaline; heating and distillation are then carried out as before. The atmosphere of the apparatus is washed with 10 ml. and then six times with 5 ml. of water each time. Atmospheric pressure is restored, the flask is disconnected, and the distillate and the washings are boiled to expel carbon dioxide. After cooling, 2 drops of a 1 per cent. solution of neutral red are added, and the excess of sulphuric acid is titrated with a 0·02 *N* solution of sodium hydroxide. If n ml. are needed, the proportion of hexamethylene-tetramine in the sample was $(20-n) \times 0{\cdot}7$ mg. Various samples examined by this method gave results varying from 98 to 100 per cent.

D. G. H.

Artificial Resins as Containers for Drugs. P. Pinten. (*Chem.-Ztg.*, **1935, 59,** 787.)—The odour of ammonia which is sometimes apparent when empty containers made from phenol plastics are opened (cf. *id.*, 1935, **59**, 636) is not due to decomposition, but to the production of ammonia from hexamethylene-tetramine during the manufacturing process. This gas appears to be retained by the surface of the resin and is evolved only slowly; it is associated chiefly with the novolac resins and, to a far less extent, with the resoles, and it may be removed by heating the resin at 140° to 150° C., a process which also produces a harder product of greater chemical stability. In general, the phenol-content of the phenol resins decreases slowly in damp air, but this decrease is very small with properly hardened resins, and gives rise to trouble only in rare cases. Thus, hot coffee made by infusion in a resin container may acquire a phenolic taste, although cold coffee will not. Neutral substances, weak acids and fats in ointments, are without influence on such containers, but strong alkalis attack them. The choice of raw materials is important to ensure stability, and when *o*- or *p*-cresol is used for cheapness, resinification may be incomplete, and the material will become distinctly soluble. It is suggested that the harmful effect of the vapours of phenol or formaldehyde may be overrated, as workers exposed to them in high concentrations develop no serious symptoms. Great care is necessary, however, in handling the resin in the powdered form, not because of the evolution of phenolic vapours, but because it affects the lungs in a manner similar to siliceous dusts. Amino plastics (*e.g.* pollopas) are probably the least objectionable of these resins, and vessels made from the polystyrol (trolitul) type are unaffected by water, acids, alkalis or alcohol. Ampoules made from it are as hygienic as glass and much stronger.

J. G.

Biochemical

Deuterium as an Indicator in the Study of Intermediary Metabolism. I. R. Schoenheimer and D. Rittenberg. (*J. Biol. Chem.*, 1935, **111**, 163–168.)—I. The use of the hydrogen isotope, deuterium, is proposed for the study of intermediary metabolic processes. The concentration of deuterium can be determined in small samples with a high degree of accuracy, and therefore the fate of a physiological substance in which some of the hydrogen has been replaced by the deuterium can be traced in the organism after administration. Stearic acid, 6–7–9–10d_4, was prepared from linolic acid by shaking 4·5 g. of methyl linolate with about 100 mg. of platinum oxide in dry petroleum spirit at room temperature in an atmosphere of deuterium for 85 minutes. The ester was saponified, and the acid was liberated and recrystallised from alcohol. It contained 10·87 per cent. of deuterium (calculated 11·11 per cent.).

II. *Ibid.*, 169–174. The deuterium is produced by the electrolysis of a dilute solution of D_2SO_4 in D_2O in the cell, *a* (see Fig. 1). The gases are dried by passing them through the traps, *b* and *c*, immersed in solid carbon dioxide. The oxygen bubbles through the mercury to the air, while the deuterium bubbles up into the bulb *d*. The gas in *d* is periodically discharged into the 5-l. storage reservoir, *e*, in which the pressure is kept less than one atmosphere. With the aid of the Toepler pump, *f*, the gas may be transferred to the reaction bulb or pumped back from the reaction bulb to the storage reservoir. The trap, *g*, is immersed in solid carbon dioxide and prevents the vapours of the solvent in the hydrogenation vessel from diffusing back into the storage reservoir, *e*. The hydrogenation is carried out in ordinary hydrogenation bulbs. The amount of gas absorbed during the hydrogenation may be calculated from the change of pressure in the system as shown by the manometer, *b*. The only rubber connection in the apparatus is between the trap, *g*, and the hydrogenation flask. Hydrogenation with deuterium must not be carried out with unsaturated substances, such as acids or alcohols, for the hydrogen would interchange with the deuterium gas in which the substance is shaken, and a part of this hydrogen would enter the double bond. In order to hydrogenate such substances, esters or other derivatives must be used. The method of determining the deuterium-content of any material is, in general, the same as that used for the determination of carbon and hydrogen in organic substances. The difference is that instead of the water formed being absorbed by a hygroscopic salt, it is frozen out by solid carbon dioxide. The oxygen passes over heated copper oxide, and is then dried by passage through a trap immersed in solid carbon dioxide. The dried oxygen is carried over the heated substance contained in the usual boat, and the water formed is frozen out in another trap, which is immersed in solid carbon dioxide. The amount of material used varied from 0·07 to 1·0 g., depending upon the probable deuterium-content. The water so obtained was then purified by the following procedure:—The trap containing the water was connected with another quartz combustion tube filled with copper oxide and heated to 750° C. A slow stream of dry oxygen carried the water vapour through the quartz tube, and the water was again frozen out in a similar trap. When all the water had been collected, a few crystals of chromic acid were added, and the trap was connected through an all-glass joint with a distillation system composed of three traps in series, the first of which contained 2 to 10 mg. of solid potassium hydroxide and a few crystals of potassium permanganate. The other two traps were empty, but the last one was connected with a two-way tap, so that a vacuum could be applied or air admitted. Air was admitted, the ice melted, and the water was gently boiled for 3 minutes. After cooling, the water was distilled *in vacuo* to the second trap. Air was again admitted, the ice melted, and the water was distilled *in vacuo* to the third trap. The concentration of deuterium was now determined. If the concentration of deuterium (in per cent.), multiplied by its weight in g., exceeded 0·2, the deuterium was determined by the difference in refractive index between H_2O and D_2O. This was done in a Zeiss interferometer, the difference being 0·00462 for the sodium D line at 20° C. If the amount of deuterium was less than this amount, it was estimated by determining the density of the water by means of a submerged-float

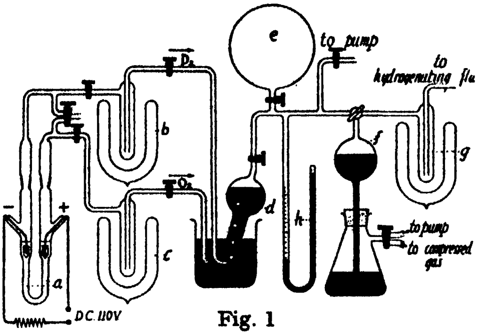

Fig. 1

method. The purified water obtained by the method described above was diluted to 2·5 ml. with pure distilled water and distilled *in vacuo* into a small tube containing a glass float which was so constructed that it just floated in water at 0° C. and at atmospheric pressure. The receiver was maintained in a bath of ice and distilled water in a Dewar flask, and attached to the neck of the receiver was a series of stopcocks by means of which the pressure inside the receiver could be varied and measured on a manometer. If the pressure was lowered, the float rose, and the time was taken for it to pass two cross-hairs in the field of a microscope. If the pressure was increased, the float fell and similar readings were taken. By plotting the velocities obtained in this way against the pressures as read on a manometer, a straight line was obtained, and the floating pressure determined. In the apparatus used, a change in pressure equivalent to 1 cm. of mercury corresponded with a change in density of 0·376 p.p.m. Since the density of pure D_2O is 1·1079, a change of 1 p.p.m. in the density corresponds with about 0·001 per cent. of deuterium.

III. *Ibid.*, 175–181. Mice were fed from 2 to 10 days on a diet composed of 20 per cent., 4 per cent., and 1 per cent. of deuterium-containing fats. At the end of this period the deuterium-content of the fat depôts, the fat of the internal organs, and the body fluids was determined. Much of the diet fat was found in the fat depôts. In experiments with mice fed for 4 days on a diet containing 1 per cent. of fat, 47 per cent. of the ingested fat was found in the depôts, and heavy water equivalent to 20 per cent. of the ingested fat in the body fluids. A small amount of the absorbed fat was found in the internal organs. These experiments indicated that, even when it is present in small quantities, the largest part of the diet-fat was deposited in the fat tissues before it was utilised.

S. G. S.

Lead-content of Human Tissues and Excreta. S. L. Tompsett and A. B. Anderson. (*Biochem. J.*, 1935, 29, 1857–1864.)—A method, which is claimed to be an accurate one, is described for the determination of lead in human tissues, blood and excreta. The material under investigation is ashed and the lead is extracted with ether as a complex with sodium diethyldithiocarbamate. The lead in the ethereal extract, after the destruction of the organic material, is determined colorimetrically with diphenylthiocarbazone. Lead was found in all the tissues examined, and the question whether this was present during life or was due to mobilisation of lead from deposits in the bones owing to metabolic changes preceding death is mentioned. The "normal" lead-content of the human body is also discussed. The recovery of lead added to serum already containing this metal varied from 90 to 120 per cent., and in a similar experiment with blood from 90 to 112 per cent. In the tissues examined the average values (in mg. Pb. per kg.) for adults were: liver 1·73, kidney 1·34, spleen 1·68, brain 0·5, rib 8·55, vertebra 7·09. Tissues from a case of known exposure to lead gave higher figures, especially for the rib, which was 119 mg. per kg. From the analysis of four foetuses of 7 to 8 months' gestation the following average amounts (in mg. per kg.) were obtained: liver 0·68, kidney 0·63, brain 0·7, and femur 1·73. Adult urine gave an average figure of 0·05 mg. per day, and faeces 0·22 mg. for the same period. Blood from three normal persons and eighteen patients, none of whom was acutely ill, was also examined, and the values obtained varied from 40 to 70γ per 100 ml., with an average of 55γ. A soldermaker who exhibited symptoms of plumbism had blood with a varying lead-content, the maximum recorded being 380γ per 100 ml. S. G. S.

Precipitation of *l*-, *dl*-, and *m*-Cystine by Phospho-12-tungstic Acid. G. Toennies and M. Elliott. (*J. Biol. Chem.*, 1935, **111**, 61–74.)—If the precipitation of the phospho-12-tungstates of *l*-, *dl*, and *m*-cystine is carried out at 0° C., and the solutions left at that temperature for several days, the reaction proceeds until nearly complete. The precipitates should be filtered off on an ice-cooled Buchner funnel and sucked dry before analysis. In the presence of *N* hydrochloric acid solution, *m*-cystine can be precipitated to a residual concentration of $5 \times 10^{-4}M$ in the presence of $2 \times 10^{-2}M$ phosphotungstic acid. The corresponding concentrations for *dl*-cystine are $1{\cdot}5 \times 10^{-5}M$ and $4 \times 10^{-2}M$, whilst for *l*-cystine these become $1 \times 10^{-5}M$ and $1 \times 10^{-2}M$. Previous statements concerning the constitution of cystine phosphotungstates were not confirmed, for in a constant medium (*N* hydrochloric acid solution) the crystalline precipitates vary in their composition according to the ratio of cystine to phosphotungstic acid used. The precipitates were examined for sulphur by a modification of the Blix potassium permanganate method, after removal of the phosphotungstic acid by amyl alcohol, and the phosphotungstic acid was determined by ignition. *l*-Cystine was also determined by the optical rotation of the phosphotungstate in acetone solution. In *N* hydrochloric acid solution, containing 31 to 32 per cent. by volume of acetone, within a concentration range of 2·5 to 4·8 g. of cystine per 100 ml., in the presence of 27 to 60 g. of phosphotungstic acid, the value for $[\alpha]^{25}_{g}$ was −236° ± 2° with a temperature coefficient of −2·2°. S. G. S.

Leaf Carotenes. G. MacKinney. (*J. Biol. Chem.*, 1935, **111**, 75–84.)—Carotenes derived from the leaves of 59 different plant species, distributed in forty botanical families were examined, and it was found that in all cases the major fraction was β-carotene. In the material from forty of these sources α-carotene was found in amounts varying from a trace up to 35 per cent. of the total carotene present. By the use of an adsorbent the presence, in traces, of another carotenoid was detected. The application of phylogenetic considerations to the prediction that leaves of closely-related plants or groups of plants would give carotene complexes which did not differ materially from one another, was fairly successful; but at present there is no adequate explanation of the presence or absence of α-carotene in any specific plant. S. G. S.

Carotenes from Different Sources and Some Properties of α- and β-Carotene. H. S. Strain. (*J. Biol. Chem.*, 1935, **111**, 85–93.)—Carotenes from a number of natural products were isolated and separated by the use of adsorption columns composed of magnesium oxide. In every instance β-carotene was the principal component of the mixtures, which often contained α-carotene, as well as other carotenoids, more strongly adsorbed than β-carotene. Material from the petals of the Californian poppy, the leaves of the white carrot, and butter contained a carotene which was less readily adsorbed than α-carotene, and which appeared to be identical with a similar carotene previously isolated from palm oil. Most sources of carotene contained colourless substances which influenced the adsorption of carotene and which often crystallised with it, even after it had been isolated by adsorption. Chlorinated solvents were then used, instead of petroleum spirit and *n*-heptane, for recrystallisation. The optical rotation of α-carotene was, in dichloroethylene $[\alpha]^{18}_{667\cdot8} = +338° \pm 10°$, in benzene $[\alpha]^{19}_{667\cdot8} = +344° \pm 10°$, in pyridine $[\alpha]^{18}_{667\cdot8} = +362° \pm 10°$, in carbon disulphide $[\alpha]^{17}_{667\cdot8} = +392° \pm 10°$; β-carotene was inactive. The difference between the two wave-lengths at maximum absorption was constant at about 30*m*μ for both isomers, and the difference between the corresponding maxima for α- and β-carotene was also constant at about 6*m*μ. The specific gravities of the isomers were identical; 1·000 ± 0·004 referred to water at 20° C. Both gave characteristic colours with antimony trichloride solution in chloroform and also with trichloroacetic acid in the same solvent. Dichloromethane and 1, 2-dichloroethane were also used for these colour tests. S. G. S.

Water

Colour-scale for the Rapid Determination of Nitrates in Water. R. Gros. (*J. Pharm. Chim.*, 1935, **127**, 244–246.)—The official colorimetric method of the Laboratoire du Conseil Supérieur d'Hygiene for the rapid determination of nitrates in water consists in evaporating in two glass capsules 10 ml. of the water under examination and 10 ml. of a solution of 0·081 g. of pure melted potassium nitrate in 1 l. of water (10 ml. are equivalent to 0·5 mg. of nitric acid), respectively, and adding to each of the cooled residues 1 ml. of a solution of 3 g. of crystallised phenol in 37 g. of sulphuric acid (sp.gr. 1·84). Five ml. of water, followed by 10 ml. of dilute (1 in 3) ammonium hydroxide, are then added, a yellow colour, due to the ammonium salt, resulting. The control corresponds with a content of 50 mg. of nitric acid per l. Colours are compared in a Duboscq colorimeter after interposition of a blue glass. A scale of stable colours may be used to eliminate the use of the colorimeter, and for this purpose a solution is used which contains in 100 ml. (*a*) dried recrystallised potassium dichromate 0·1 g.; (*b*) nickel sulphate ($NiSO_4.7H_2O$), 2 g.; (*c*) 10 drops of concentrated sulphuric acid. The scale corresponds with 10 to 50 mg. of nitric acid, when the following solutions are used:—for 10 mg. of nitric acid, 2 ml. of $a + b$, 14 ml. of *c*; for 20 mg., 40 ml. of $a + b$, 12 ml. of *c*; for 30 mg., 6 ml. of $a + b$, 10 ml. of *c* for 40 mg., 8 ml. of $a + b$ and 8 ml. of *c*, and for 50 mg. 10 ml. of $a + b$, 6 ml. of *c*. By interpolation, nitrates in water may be estimated within 5 mg. per l.

D. G. H.

Agricultural

Selenium in Soils in Relation to its Presence in Vegetation. H. G. Byers and H. G. Knight. (*Ind. Eng. Chem.*, 1935, **27**, 902–904.)—Selenium occurs in soils to a varying extent, and in certain localised areas it is present in quantities sufficient to render vegetation toxic. So far, the soils found to contain serious quantities of selenium are heavy clays which have developed from shale deposits of the Cretaceous period. The primary source of the selenium appeared to be iron pyrites or other sulphide minerals containing selenium. No sandy soils contained more than a trace of selenium. Various factors connected with entry of selenium into plants have been examined. The capacity of different plants to absorb selenium varied considerably. Thus with a one square-mile plot of land in S. Dakota the following results were obtained for the selenium-content of soil and vegetation:

Material	No. of samples	Selenium (p.p.m.) range	mean
Soil (surface)	122	0·7–13	4·8
Wild aster	1	—	2670
Western wheat grass ..	12	—	20
Little bluestem ..	50	—	0·8
All vegetation	137	—	36

It was also found, for example, on experimental plots in Wyoming, that, whereas the soil contained about 2 p.p.m. of selenium, vegetation contained selenium as follows (p.p.m.): Mixed grasses, 10; *Astragulus missouriensis*, 3; *A. bisulcatus*, 1250. Some plants, therefore, are highly absorptive of selenium. These results were obtained with plants grown under relatively dry conditions, and there are indications that, on well-watered soils, contamination of plants by selenium is minimised by reason of the selenium being washed out of the surface layers of the soil. Thus, irrigation in dry areas might be a remedy for the selenium trouble, and this point is to be further studied. The distribution of selenium in the plants is irregular, and, in general, more selenium is found in the leaf than in the stem or seed. Thus, wheat leaves in a given sample contained 40 p.p.m. of selenium, whilst the stalks and grain contained 12 p.p.m. and 8 p.p.m., respectively. In seleniferous wheat the selenium is largely concentrated in the wheat gluten. S. G. C.

Determination of Base-Exchange in Soils by means of Copper. J. Lavollay. (*Ann. Chim. anal.*, 1935, 17, 229–230.)—Fieger, Gray and Reed (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 281) treated the soil with copper nitrate solution. The amount of copper rendered insoluble by the soil was found indirectly by determination of the diminution in strength of the copper solution. It is now pointed out that this procedure does not give a true value of the base exchange of soils containing calcium carbonate, because some copper is thereby precipitated as basic copper carbonate. It is therefore preferable to determine directly the copper precipitated as a result of base exchange, as in the following method, which involves acting on the soil, after copper nitrate treatment, with sodium acetate solution; the basic copper carbonate remains undissolved, whilst the copper absorbed in the soil becomes replaced by sodium and re-dissolves, and may be determined in the sodium acetate extract by precipitation with 8-hydroxyquinoline. *Method.*—To 25 g. of the fine soil are added 200 ml. of copper nitrate solution (10 per cent.), and the mixture is kept for 24 hours, with occasional shaking. The soil is filtered off on a Buchner funnel and washed with alcohol. About 200 ml. of sodium acetate solution (14 per cent.) are poured slowly over the soil on the funnel. An aliquot part of the filtrate containing the extracted copper is acidified with acetic acid and boiled to remove alcohol. The *p*H value is adjusted to about 5·4 (reddish colour with methyl orange), and the copper is precipitated from the hot solution by 8-hydroxyquinoline. The precipitate is filtered off, washed with hot water, dried at 105° C. and weighed as $(C_9H_6ON)_2Cu$. S. G. C.

Organic

Determination of Methyl Alcohol in Alcoholic Products. J. B. Wilson. (*J.A.O.A.C.*, 1935, **18**, 477–488.)—The various methods which have been proposed for the determination of methyl alcohol in presence of ethyl alcohol are discussed. Those depending on oxidation of the methyl alcohol to formaldehyde are regarded as of doubtful value, owing to the uncertainty of the oxidation being complete. Flanzy's method (Abst., ANALYST, 1935, 632) is tedious, as it involves several operations, including two determinations, and a small error in either of these would considerably affect the results. In the method now described, as in that of Flanzy, the methyl and ethyl alcohols are converted into the corresponding iodides, which are partially separated by fractionation and are then converted respectively into tetramethylammonium iodide and trimethylethylammonium iodide by the action of trimethylamine. The first of these quaternary iodides is then separated by precipitation from absolute alcohol, in which it is only very sparingly soluble, and is weighed in a sintered glass crucible. The details of the procedure to be followed are described. Sugars and other substances which use up iodine interfere, but may be eliminated by distillation. Methyl esters and ethers and other compounds containing a methoxy group form methyl iodide and should be removed beforehand. Vanillin and other non-volatile constituents are removable by distilling the alcohols. Methyl esters and ethers are volatile and may be expelled by the procedure recommended by Thorpe and Holmes; a modification of this is now described. Results obtained by applying the method to samples of known composition and to various alcoholic beverages are given. T. H. P.

Use of Kaolin in the Method for Determining Non-tannins. A. Jamet. (*J. Int. Soc. Leather Trades Chem.*, 1935, **19**, 394–395.)—Baldracco's recent statement, to the effect that the use of kaolin in the determination of non-tannins introduces error, owing to adsorption of vegetable non-tannins by the kaolin, is examined. It is found that the non-tannins obtained by the Baldracco-Darmstadt method contain soluble protein substances, owing to inadequate washing of the dry hide powder. When the official method is used, in conjunction with the Jamet and Darmstadt apparatus and without kaolin, the non-tannins obtained are free from all traces of protein. T. H. P.

Volumetric Determination of Camphor by the Hydroxylamine Method. R. Vandoni and G. Desseigne. (*Bull. Soc. Chim.*, 1935, **2**, 1685–1691.)—In the modification proposed by the authors, 50 ml. of 2 *N* hydroxylamine hydrochloride are introduced into a 100-ml. flask having a ground-in reflux condenser. After addition of 0·2 ml. of the indicator the solution is brought to the same colour as a standard prepared by dissolving 7 g. of hydroxylamine hydrochloride in 25 ml. of water and 40 ml. of 95 per cent. alcohol, adding 0·2 ml. of a 1 per cent. alcoholic solution of bromphenol blue, and bringing the mixture to the neutral point (green) by adding 0·3 ml. of *N* sodium hydroxide solution. One g. of sodium carbonate (accurately weighed) is added, and 1 to 2 g. of the substance to be analysed. The mixture is boiled gently for about 1 hour under the reflux condenser on a water-bath, and then allowed to cool to about 30° C. At the end of the reaction the solution should still be alkaline to bromphenol blue. *N* hydrochloric acid is then run in from a burette until the solution is distinctly yellow, and, when the sodium carbonate is entirely dissolved, the liquid is titrated back to the standard colour with *N* sodium hydroxide solution. Since hydroxylamine hydrochloride is slowly decomposed when boiled in dilute alcoholic solution with sodium carbonate a correction factor must be applied, 0·0003 mol. being deducted from the number of mols. found by titration. The method also gave satisfactory results with carvone, menthone and camphylene, but with fenchone the results were about 6 per cent. too low. The procedure may also be applied to the determination of camphor in organic liquids not miscible with water. A little absolute alcohol may be added at the time of titration to obtain a homogeneous solution, though the end-point can be observed in a heterogeneous mixture. Finally, the method may be used for the determination of camphor in nitrocelluloses after saponification, the aqueous solution being extracted with a suitable solvent. A. O. J.

Inorganic

Use of 8-Hydroxyquinoline in the Determination of Aluminium, Beryllium and Magnesium. H. B. Knowles. (*Bur. of Standards J. Research*, 1935, **15**, 87–96.)—Aluminium can be quantitatively precipitated and separated from beryllium and magnesium at *p*H 6·8. *Method* (*a*). *In absence of beryllium.*—To the solution (200 ml.), containing about 10 ml. of hydrochloric acid, tartaric acid is added in amount equal to 5 times the weight of aluminium present.* Fifteen ml. of ammonium acetate solution (30 g. of ammonium acetate dissolved in 75 ml. of water) and 8 to 10 drops of bromocresol purple indicator (0·04 per cent.) are added, followed by dilute ammonia until the indicator changes to purple. The solution is stirred, and a solution of 8-hydroxyquinoline in dilute acetic acid (12·5 g. of 8-hydroxyquinoline dissolved in 25 ml. of hot glacial acetic acid and diluted to 500 ml. and filtered) is added slowly in 15 to 25 per cent. excess. The liquid is heated to boiling, with occasional stirring, and boiled for 1 minute. After being allowed to cool to 60° C., the precipitate is filtered off on a sintered glass crucible of fine porosity (*e.g.* 1bG4), and washed with 100 ml. of cool water. The determination may be finished gravimetrically by drying the precipitate for 3 hours at 135° C., and weighing as $Al(C_9H_6ON)_3$, which contains 5·87 per cent. of aluminium or 11·10 per cent. of aluminium oxide. For volumetric determination, the crucible and contents are heated in a beaker containing 200 ml. of dilute hydrochloric acid (1 + 4) until the precipitate has dissolved; the crucible is removed, washed with dilute (1 + 9) hydrochloric acid, and the washings are added to the main solution, which is diluted to 400 ml. and cooled. Standardised potassium bromate-bromide solution (0·1 *N* solution should be used for amounts of aluminium up to 10 mg., and *N* solution for amounts such as 50–100 mg.; *N* solution contains 27·835 g. of potassium bromate and 100 g. of potassium bromide per l.) is added in moderate excess (2 to 3 ml.) as determined by test after allowing 1 minute for complete bromination of the hydroxyquinoline (1 drop is withdrawn and added to a drop of potassium iodide and starch solution on a spot plate, a blue colour indicating an excess); 15 ml. of 20 per cent. potassium iodide solution are added, and the liberated iodine is titrated with standard sodium thiosulphate solution, starch being used as indicator; 1 ml. of *N* bromate-bromide solution ≡ 0·0022475 g. of aluminium. It was found in test experiments that accurate results (within a few tenths of a mg.) were obtained only when the amount of aluminium taken was not more than 25 to 50 mg.; with larger amounts there was a distinct positive error due to retention of the reagent in the precipitate; the error was more marked in the volumetric than in the gravimetric method. For accurate results with amounts of aluminium exceeding 50 mg., the following procedure is recommended: The oxyquinolate precipitate is dissolved in dilute sulphuric acid, the solution is evaporated "to fumes," and the organic matter is destroyed by the addition of nitric and perchloric acids; the aluminium is subsequently determined by precipitation as hydroxide in the usual way.

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* Abstractor's Note.—No statement is made that the amount of tartaric acid is critical.

Method (*b*). *In presence of beryllium.*—The method is the same, except that tartaric acid is omitted. The beryllium may be determined in the filtrate by precipitation with ammonia in the usual manner; the excess of hydroxyquinoline present does not interfere with the precipitation of the beryllium provided the solution is allowed to cool before filtration. Test experiments showed that with up to 0·1 g. of aluminium and beryllium present the aluminium precipitate contained a maximum of 0·1 mg. of beryllium. The results for aluminium were not so good as were obtained by Method (*a*) (when tartaric acid was present), owing to somewhat greater co-precipitation of reagent.* *Separation from magnesium.*—The aluminium oxyquinolate precipitated in the presence of up to 0·1 g. of magnesium in solution by either Method (*a*) or (*b*) was found to retain less than 0·2 mg. of magnesium. *Determination of aluminium in felspar.*—Iron, titanium and other interfering elements are in general present in such small quantities as to make their prior removal unnecessary in ordinary work, and rapid routine determinations of alumina can be made by precipitating the aluminium from a solution obtained from 0·1 g. of feldspar after removal of silica. *Interfering elements.*—Numerous elements interfere in the above processes, such as the heavy metals, manganese, alkaline earth metals, iron, titanium and zirconium.

S. G. C.

Hexammine Cobaltic Compounds of Vanadium. W. G. Parks and H. J. Prebluda. (*J. Amer. Chem. Soc.*, 1935, 57, 1676–1678.)—Parks ("Dissertation," Columbia University, 1930) found that the hexammine cobaltic ion reacted with quinquevalent vanadium solutions to yield the following: (*a*) in neutral solution: an apricot-coloured precipitate of hexammine cobaltimetavanadate;

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* Abstractor's Note.—It is to be presumed that Method (*a*) would be satisfactory for separating aluminium from beryllium if determination of beryllium in the filtrate were not required.

(*b*) in alkaline solution: an orange-coloured precipitate of hexammine cobaltipyrovanadate; (*c*) in a solution buffered with acetic acid and ammonium acetate at *p*H 5·1: a yellow precipitate of hexammine cobaltideuterohexavanadate. These findings have been verified in the present investigation. Parks also found that in the acid medium, the vanadium was precipitated quantitatively and could thus be separated quantitatively from phosphate, arsenate, and ferric, cupric and calcium ions, but not from tungstate, molybdate or lead ions. No tests of these further statements were carried out by the present authors. S. G. C.

Detection and Determination of Gold by means of Carbon Monoxide. R. N. Costeanu.—(*Z. anal. Chem.*, 1935, **102**, 336–338.)—Solutions of gold chloride are reduced to colloidal gold by carbon monoxide; a filter paper soaked in a gold solution turns purple in a stream of the gas. The colour increases in intensity with the gold concentration. For a colorimetric determination of gold in an alloy, the filings (0·025 g.) are first extracted with nitric acid; the insoluble residue is dissolved in *aqua regia*, the liquid is evaporated, and the chloride is dissolved in 25 ml. of water. Strips of filter-paper are moistened with the solution, allowed to drain, and placed in a horizontal glass tube. In a parallel tube are placed strips of paper impregnated with gold solutions of known concentration (*e.g.* 1, 0·5, 0·25, etc., mg. Au per ml.). The tubes are connected with a generator containing formic and sulphuric acids; the carbon monoxide is dried over phosphorus pentoxide before passing over the test-papers. W. R. S.

Determination of Chromium in Chrome-tanned Leather. G. F. Smith and V. R. Sullivan. (*J. Amer. Leather Chem. Assoc.*, 1935, **30**, 442–453.)—The method involves destruction of the leather and oxidation of the chromium by wet oxidation with perchloric acid, and titration of the chromic acid formed. The digestion process may be accelerated by means of catalysts such as vanadic acid or osmic acid. *Method.*—To a 1-g. sample of the leather contained in a 500-ml. conical flask are added 15 ml. of oxidising solution (2 vols. of 70 per cent. perchloric acid and 1 vol. of sulphuric acid, sp.gr. 1·73) and 5 ml. of concentrated nitric acid. The mouth of the flask is closed by a thistle funnel having a sealed off stem bent so as to touch the inside surface of the flask. The liquid is digested at a temperature between 175° and 200° C., at which it boils quietly. When oxidation is complete, the solution is cooled somewhat by dipping the flask (after giving it a rotatory motion) in cold water for 4–5 sec., diluted with 30 to 40 ml. of water, and boiled 2 to 3 minutes to remove chlorine. The solution is further diluted to 200 ml., cooled, 1 ml. of 85 per cent. phosphoric acid and a few drops of sodium diphenylamine sulphonate indicator solution (0·005 *M*) are added, and the chromic acid is titrated with 0·05 *N* ferrous sulphate solution until the initial purplish colour changes to light green. *Use of catalyst.* (*a*) *Osmic acid.*—The procedure is the same as that above, except that approximately 0·2 ml. of 0·01 *M* osmic acid solution is added with the mixed acids at the start of the digestion process. (*b*) *Vanadium.*—About 30 mg. of ammonium vanadate are added in the digestion process. The following modified procedure for titration is required:—instead of the diphenylamine sulphonate indicator, 2 drops of *o*-phenanthroline ferrous sulphate solution (0·025 *M*) are added, followed by a slight excess of 0·05 *N* ferrous sulphate solution (indicator colour changes to intense pink); 20 to 25 g. of sodium acetate trihydrate are added, the solution is heated to 50° C. and titrated with either 0·05 *N* ceric sulphate solution or 0·05 *N* potassium permanganate solution (grey to light bluish-green colour at end-point). Test experiments showed that an accuracy of ±0·02 per cent. may be expected. Vanadic acid is a somewhat more efficient catalyst than osmic acid. Various leathers required 18 to 41 minutes for destruction of organic matter without the use of catalyst, 17 minutes with osmic acid catalyst, and 11 to 16 minutes with vanadium catalyst; the leathers containing paraffin filling-materials required the longer time. S. G. C.

Determination of Vanadium in Uranium Salts. N. I. Tscherwjakow and E. A. Ostroumow. (*Z. anal. Chem.*, 1935, **102**, 181–186.)—The principle of the method consists in the oxidation of dimethyl-*p*-phenylenediamine by quinquevalent vanadium. The uranyl salt (sulphate or chloride; 0·2 to 0·5 g.) is dissolved in a minimum of water in a Nessler tube. Uranyl nitrate or acetate must first be converted into chloride. The tube serving for the colour standard contains an equivalent amount of pure uranium solution. The two solutions are treated with 5 to 6 drops of hydrochloric acid (1 : 1), 0·5 ml. of phosphoric acid, and at least four times the total volume of the liquid in alcohol; the total volume before this addition should not exceed 10 ml. Glycerin (3 to 4 ml.) is added, and the solutions are well stirred. The above procedure converts any ferric salt present into a stable complex glycerin ester. If the solution becomes cloudy at this point, it is cautiously treated with dilute hydrochloric acid until clear; the standard should be treated exactly like the assay. One ml. of a 0·5 per cent. solution of the base (sulphate or hydrochloride) is added to each tube, and they are shaken for half a minute. The red tinge of the unknown solution is then matched by titration of the standard with a vanadate solution of known strength. Four minutes are allowed to elapse before the final adjustment is made. The method may be applicable to the determination of minute amounts of vanadium in other preparations. If the iron-content is high, previous fusion with sodium carbonate is necessary. W. R. S.

Volumetric Determination of Iodide with an Iodine-Starch Indicator. E. Chirnoaga. (*Z. anal. Chem.*, 1935, **102**, 339–342.)—The method of Kolthoff (*Pharm. Weekbl.*, 1917, **54**, 761) consists in the addition of a little iodate (or iodine) and starch solutions to the slightly acidified iodide solution, and titration with silver nitrate. The author avoids introducing an iodine compound by the following modification. The neutral or acid (10 ml. of 0·1 *M*) solution is treated with 2 drops of saturated ferric sulphate solution and 2 ml. of 0·4 per cent. starch solution, and titrated with 0·1 *N* silver nitrate solution. The colour changes from blue to green, the precipitate adsorbing the blue starch compound. The precipitate appears orange immediately before, and characteristically yellow at, the end-point. In presence of chloride, 10 ml. of 2 *M* sodium acetate solution must be added with the ferric sulphate and starch solutions. The procedure permits of the determination of the chloride also; the silver iodide is filtered off and washed three times with water. The filtrate is treated with 2 to 3 ml. of ferrous ferricyanide indicator (Abstr., ANALYST, 1935, 428), and titrated with silver nitrate solution until the precipitate is colourless. If bromide also is present, the titration must be carried out in ammonium carbonate solution, as prescribed by Kolthoff. W. R. S.

Determination of Fluorine in Phosphorites by a Simplified Method. S. N. Rosanow. (*Z. anal. Chem.*, 1935, **102**, 328–336.)—The apparatus and technique applied in Penfield's evolution method have been simplified, with the result that a determination can be carried out in about four hours. The original paper gives constructional and manipulative details. W. R. S.

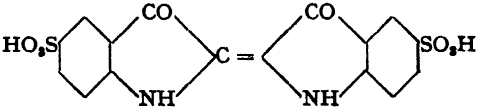
New Method for the Separation of Selenium from Sulphur. E. Cheraskowa and L. Weissbruth. (*Z. anal. Chem.*, 1935, **102**, 353. Preliminary communication.)—The method is based upon the differential stability between thiosulphate and selenothiosulphate, the latter only being decomposed by formaldehyde, with precipitation of selenium. The weighed substance, containing the two elements as such, is boiled under reflux with 100 ml. of 10 per cent. sodium sulphite solution for two hours. The cold extract is filtered, and the filtrate is treated with 50 ml. of formalin added through the reflux condenser. The selenium is precipitated on heating. It is collected after standing overnight, washed with cold water, hydrochloric acid (1 : 1) for the removal of any ferric oxide, then with hot water, and finally with alcohol and ether. The dried precipitate is weighed. The filtrate from the selenium is treated with 20 ml. of 20 per cent. acetic acid, and the thiosulphate is titrated with 0·1 *N* iodine solution.
W. R. S.

Gravimetric Determination of Selenate. R. Ripan-Tilici. (*Z. anal. Chem.*, 1935, **102**, 343–344.)—Lead selenate is more advantageous for gravimetric purposes than the barium salt, being more insoluble and crystalline. The boiling selenate solution (about 0·01 *M*) is treated, drop by drop, with a 0·5 *M* lead nitrate solution (0·1 to 0·2 ml. excess). The solution is kept boiling for a few seconds, and treated with enough alcohol to provide 30 to 35 per cent. in the liquid. The covered beaker is kept 4 to 5 hours at room temperature with occasional stirring. The precipitate is collected in a porous porcelain crucible and washed, by decantation first, with 30 per cent. alcohol. It is finally washed with strong alcohol, then ether, kept *in vacuo* for a short time, and weighed. A large excess of precipitant must be avoided, as lead selenate has a strong adsorptive power.
W. R. S.

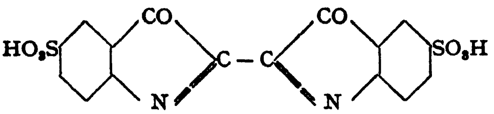
Microchemical

Chemical Microscopy of Gold and the Platinum Group. W. F. Whitmore and H. Schneider. (*Mikrochem.*, 1935, **17**, 279–319.)—The crystalline reactions of the elements were studied, by the usual methods of chemical microscopy. The elements tested were used in solutions of 1, 2 and 5 per cent. concentrations, and the reagents at 10 per cent. concentration, except the alkaloids, which were used in 1 per cent. solutions; when crystals did not form readily, as frequently happened, the reagent was used in the solid form. A large number of reactions are given with illustrations of some of the crystals formed. The most characteristic reactions for each metal take place with the following reagents:—*Ruthenium*: (1) Tetraethyl-ammonium bromide, (2) methylamine hydrochloride. *Rhodium*, no satisfactory reagent. *Palladium*: (1) Dimethylglyoxime, (2) caffeine: *Osmium* must be separated by distillation, when crystals may be formed with potassium hydroxide. *Iridium*: (1) Methylamine hydrochloride. *Platinum*: (1) Meta-toluidine hydrochloride, (2) meta-phenylenediamine, (3) diethylamine hydrochloride. *Gold*: Caffeine. A method for the microscopic analysis of the group has been developed: in this method it is advisable first to separate gold from the rest of the group by extraction with ethyl acetate, and then osmium by distillation; the other metals (with the exception of rhodium) are then detected by testing with the reagents listed above. J. W. M.

Use of Indigo Carmine in Micro-volumetric Analysis. I. M. Korenman (*Mikrochem.*, 1935, **18**, 31–38.)—By oxidation under suitable conditions, indigo carmine (I), which forms a blue solution, gives the yellow compound disulphodehydro indigo (II).



(I)



(II)

To prepare a 0·01 N solution, 2·3311 g. of the sodium salt of indigo carmine, or 2·1111 g. of the free acid, are dissolved in water and the solution is diluted to 1000 ml. This solution should be diluted freshly each day to 0·001 N, as the weaker solutions do not keep. For titrations in alkaline solutions, the indigo carmine is standardised against 0·01 N potassium ferricyanide, 2 ml. of ferricyanide and 1 ml. of concentrated sodium carbonate solution being used. The colour-change from yellow to green marks the end of the titration. For titrations in acid solutions, the indigo carmine is standardised against 0·001 N potassium permanganate solution, the end-point being the yellow colour in the colour-change blue—green—yellow. Standardisation by either method gives the same result. Permanganate, ferricyanide and iron may be determined by means of indigo-carmine titrations, and, conversely, indigo carmine itself may be determined. On amounts of potassium ferricyanide varying from 0·8 to 0·016 mg. the results differed from the calculated amounts by less than 2 per cent. Slightly greater errors, up to a difference of 4 per cent., were obtained in determinations in the presence of large amounts of foreign substances. It has been shown (Mika, *Z. anal. Chem.*, 1929, **78**, 268) that the accuracy of the micro-permanganate titration of iron depends on the size of the indicator correction. For a 0·001 N permanganate solution this is about 0·12 ml. for a final volume of 5 ml. For indigo carmine it is only 0·03 ml. for a final volume of 5 ml. Therefore it is more accurate than the direct permanganate titration to reduce the excess of permanganate by a known volume of indigo carmine, and to titrate back with permanganate. The iron may also be determined directly by means of 0·001 N indigo-carmine solution and a weak solution of potassium permanganate. Fairly good results were obtained in the determination of very small amounts of iron, varying from 7 to 100γ; on 7γ the error was 20 per cent., and on 15 to 100γ it was of the order of 5 per cent.

J. W. M.

Microchemical Colorimetric Determination of Sodium. A. Elias. (*Anales Asoc. Quím. Argentina,* 1935, 23, 1–3.)—In this method the sodium is precipitated as the triple acetate of uranium, sodium and magnesium, and the uranium in the precipitate is determined colorimetrically. To prepare the reagent, two solutions are made: (1) 50 g. of uranium acetate are dissolved in 30 ml. of glacial acetic acid and the volume is made up to 250 ml. with water; (2) 165 g. of magnesium acetate are dissolved in 30 ml. of glacial acetic acid, and the volume is made up to 250 ml. (presumably with water). The two solutions are mixed, and the mixture is left for a few days and then filtered. An approximately 2 per cent. sodium salicylate solution is also required. The colour is finally matched against that obtained with 0·1 N sodium hydroxide solution.

Of the solution to be tested—which should contain 0·001 to 0·002 g. of Na_2O per ml.—1 ml. is treated in a small beaker with 5 ml. of the reagent. In another beaker 1 ml. of 0·1 N sodium hydroxide solution is acidified slightly with glacial acetic acid and treated with 5 ml. of the reagent. Precipitation is induced by rubbing the walls of the beakers rapidly with a glass rod, and the beakers are left for 24 hours in an ice-chest. Each solution is then treated with its own volume of alcohol and, after 20 minutes, is filtered by decantation. The precipitates are washed three or four times with alcohol, the last runnings of which should, after dilution with water, give no reaction with the sodium salicylate solution. The precipitates in the beakers and on the filters are freed from alcohol by means of a current of air and are then dissolved in water to a volume of 50 ml. Five ml. of each are treated with 5 ml. of 2 per cent. sodium salicylate solution and the colour intensities are matched by suitable dilution.

This procedure allows of the rapid determination of sodium in 10 ml. of water, which may need concentration to 1 ml. if the mineral-content is low. Potassium is not precipitated by the reagent if its concentration, as chloride, is below 20 per cent.; precipitation of lithium begins when 11 per cent., as chloride, is present. Free mineral acids should be absent, and any phosphate or arsenate should be removed beforehand.

T. H. P.

Elimination of Phosphoric Acid in Qualitative Micro-analysis. S. Ginsburg and M. H. Pringsheim. (*Bull. Soc. Chim.*, 1935, 2, 1694–1697.)—The method is based upon the observation of Willstaetter (*Ber.*, 1924, 57, 1088) that phosphoric acid can be separated from aqueous solutions by means of certain colloids such as aluminium B hydroxide and colloidal ferric hydroxide. The separation may be carried out suitably in a medium of $N/10$ acetic acid. For 10 ml. of a solution of potassium dihydrogen phosphate (0·05 per cent. of P_2O_5) in $N/10$ acetic acid, it is necessary to use 10 ml. of a suspension of colloidal ferric hydroxide containing 6 mg. of Fe_2O_3 per ml., and to shake the mixture for a few minutes at the ordinary temperature. The method can also be used at higher concentrations; thus, 8 ml., containing 25 mg. of P_2O_5 and 0·5 ml. of glacial acetic acid, were treated with 8 ml. of a solution of colloidal ferric hydroxide containing 120 mg. of ferric oxide, and afterwards with 4 ml. containing 60 mg. of ferric oxide. This procedure effected complete elimination of phosphoric acid. In experiments in which certain other metallic salts (sulphates of nickel, manganese, chromium, aluminium, zinc) were also present, the phosphoric acid was eliminated by the procedure described, except from the solution containing chromium sulphate, with which it was necessary to increase the quantity of precipitant. Zinc phosphate was precipitated only at higher concentrations on addition of $N/10$ ammonium acetate solution. After elimination of phosphoric acid from the solutions containing iron and aluminium sulphates these metallic cations were not present in the solution. Nickel and manganese remained in the solution after the phosphoric acid had been removed. Zinc also remained in solution, but in smaller amount.

A. O. J.

New Test for Phosphate and Arsenate. L. W. Marrison. (*Chem. and Ind.*, 1935, **54**, 872).—One drop of the test solution is placed on filter-paper with 1 drop of sodium sulphide solution ($N/50$). A drop of ammonium molybdate solution (2·5 per cent.) acidified with sulphuric acid is placed near the first drop so that the solutions join. Molybdenum-blue forms instantaneously in the presence of orthophosphate, pyrophosphate, metaphosphate, or arsenate; the limit of sensitiveness is 0·0005 mg. If only small amounts of phosphate are present, the blue can be seen only at the junction of the drops or at the periphery of the brown molybdenum sulphide stain which also forms. Thiocyanate, ferrocyanide and ferricyanide should be absent, or present only in minute proportion compared with the phosphate.

S. G. C.

Physical Methods, Apparatus, etc.

Measurement of Ultra-violet Radiation in Daylight. J. S. Owens. (*Lancet*, 1935, **229**, 589–590.)—The principle used is that of an optical wedge which admits graduated quantities of light through a number of holes in an opaque plate to a sensitive paper. The use of an actual wedge is, however, open to the objection that its optical properties are not permanent, constant and reproducible. The difficulty is overcome by the use of 13 blackened tubes (diameter 0·5 inch) arranged in concentric circles and all the same height (about 6 inches). The tops of the tubes terminate in holes which vary in diameter from 0·7 to 10 mm., but the lower ends are closed by plates, each of which has a hole 3/16 inch in diameter in the centre of the base of the corresponding tube. A No. 14 Chance filter is placed over the top (to ensure that only light between 300 and 400$m\mu$ is transmitted to the apparatus) and a piece of Kodatone paper is held against the underside of the perforated plate at the bottom. On exposure to light, therefore, a number of spots are produced on the paper, and the density of each is proportional to the amount of light received, and this itself is proportional to the area of the corresponding top-hole. The scale is designed for an exposure of one whole day, since the brightest and longest day just gives a spot under the smallest hole, whilst the dullest or shortest day produces a similar effect through the largest hole. It is only necessary, therefore, to count the number of spots visible after 24 hours, and this number, referred to a scale, gives a measure of the required intensity; the paper should be inspected without fixing, as this causes fading. Advantages are robustness, waterproofness, no necessity for calibration (and this enables results obtained with different instruments to be compared), the personal factor is almost eliminated, and there is no variable wedge. It is preferable to measure only sky-light, and to this end the instrument is mounted at 45° pointing north (or at the zenith in this country). It may, however, be used to measure sunlight, and it is then advisable to use a ground or diffusing surface on the ultra-violet filter. In this connection it is interesting to note that ultra-violet radiation from the sky is often actually increased by the presence of clouds which reflect sunlight. Data are given which demonstrate the rapidity with which the intensity of ultra-violet light, as measured by this instrument, falls off as the instrument is brought nearer a building or tree which cuts off sky-light. J. G.

Photography of Fluorescent Minerals. W. M. Thornton and M. N. Lewis. (*Bull. Soc. Franc. Minéralogie*, 1934, **57**, 268–269.)—The specimen is placed on a black background in a darkened room and illuminated by means of a mercury-vapour lamp at a suitable angle. A filter (*e.g.* Hanovia Sc. 2682) is placed between the lamp and the object to eliminate visible light, and another (*e.g.* Corning Noviol C or Wratten K2) between the object and the camera to allow the passage of the fluorescent light but not the ultra-violet light reflected by the object. The optimum exposure is determined by trial and error. Among other applications in mineralogy the method may be used to examine substances responsible for lack of homogeneity in minerals; to aid investigations on mineralogical composition by planimetric integration; and to facilitate microscopical investigations of structure, especially of polished surfaces. The radioactivity of certain minerals (*e.g.* Mexican samarskite) has been used in a similar way. Photographs illustrate autunite disseminated in porphyry (from Foley Mountain, S. Dakota) in the light of an ordinary incandescent lamp and in ultra-violet light; in the latter case the porphyry only is visible, and appears as bright spots. A zinc mineral (from Franklin Furnace, New Jersey) is also illustrated. In ordinary light two veins (willemite and a rose-coloured mineral, probably manganiferous calcite) appear dirty white, and the remainder of the specimen has the usual appearance of willemite when associated with franklinite. In ultra-violet light the willemite appears green to yellow, and the other fluorescent minerals are rose-coloured; the filter allows the passage of the former, which appears white in the photograph, but absorbs most of the latter.

ABSTRACTOR'S NOTE.—The colour and intensity of the fluorescence of willemite vary considerably according to the locality in which the mineral is found.

J. G.

Reviews

HANDBUCH DER LEBENSMITTEL CHEMIE. Edited by A. BÖMER, A. JUCKENACK and J. TILLMANS. Vol. II, Part 2. Pp. 537–1726. Berlin: Julius Springer. 1935. Price 145 RM. (bound 148.60 RM).*

This substantial volume continues the style of Part I noticed in THE ANALYST (1934, 59, 440), and treats of chemical and biological methods of general application in relation to nitrogen compounds, serological methods, enzymes, carbohydrates, acids, dyes, poisons, vitamins, bacteriology and mycology. The treatment, though encyclopaedic and abounding in original references, is concise, and shows evidence of discrimination born of experience.

Food chemistry has suffered a severe loss by the untimely death of Prof. Tillmans of Frankfurt, one of the editors of these volumes. Tillmans was a most able active investigator, and many volumes of the *Zeitsch. Unters. Lebensmittel* bear witness to his industry and genius; few men could be better fitted to undertake the production of the great treatise now being issued, and we may perhaps be permitted to offer a sympathetic tribute to the editors at the loss of so distinguished a colleague whose name was esteemed here as well as in Germany. An obituary of Tillmans appears in the *Zeitsch. Untersuch. Lebensmittel*, Vol. 65, at p. 209.

Drs. Bömer, Grau and Täufel contribute the first sections on the determination of the elements and of water; every good method, including micro methods, applicable to foods seems to have been included. Then follows a longer section by Dr. Bömer on nitrogen compounds (including general and specific protein determinations), amino-acids, amines, ammonia, nitrates and nitrites; it is thoroughly up-to-date, and includes recent work on amino acids as well as details such as methods (Pluckers) for determining nitrites and sulphites present together. Professor Griebel follows with a chapter on serological methods; he explains first the theory, then the technique, as applicable to the detection of horseflesh in sausages and the identification of other kinds of flesh and fish. Progress in this branch is slow, and difficulties arising from cooking have yet to be overcome, but the methods are shown to be applicable to milk, plant and egg proteins, as well as to caviare and honey.

Drs. Waldschmidt-Leitz and Balls contribute 120 pages of sound and valuable matter on enzymes. Carbohydrates, by Professor Grossfeld, occupy 130 pages. Methods are given for the determination of every kind of sugar, including pentoses and polysaccharides occurring in foods. But it is surprising that among the many methods cited the elegant and much-used methylene blue process, for which we are indebted to Lane and Eynon, is not given. Perhaps this method and the chloramine-T method are destined to appear in later volumes under particular foodstuffs. Crude fibre, lignin, cutin, pentosans, pectins and glucosides are well treated. Alcohols, aldehydes, including two useful pages on diacetyl, organic acids and the mineral constituents of foods, are dealt with in about 300 pages (by Drs. Bömer and Windhausen), which are packed with useful matter, though we notice some omissions of good methods. In general, the writers have included the best work from all parts of the world, and the references are to original sources, as well as German abstracts.

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* According to a circular recently received, it appears that a reduction of 25 per cent. has now been made in the export price of this and other German books.

The next section is somewhat novel in a book on foods; it comprises 170 pages, from the pen of Professor Gronover, on the detection of poisons. It deals with the examination of food or viscera for metals, organic poisons, alkaloids, ptomaines and drugs. Perhaps it is a sign of the times that there is a chapter on the mathematical treatment of experimental results, showing probable errors; it comes before a section on vitamins and their assay by Messrs. Scheunert and Schieblich. Lastly, there is a good chapter on the bacteriology and mycology of foods by Professor Griebel; this would be even more interesting if it dealt more specifically with food-poisoning and its causes, rather than with general bacteriological technique, for which we are accustomed to turn to special text-books.

The work, as a whole, is extremely thorough and deserves high commendation. The price reduction recently notified is particularly welcome, but, even so, the cost of the series is very much higher than that of the best English and American scientific books.

H. E. Cox

ORGANIC SYNTHESES: AN ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Vol. XV. Pp. v + 104. Editor: W. H. CAROTHERS. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1935. Price 8s. 6d. net.

This, the latest volume of this series of annual publications, gives directions for the preparation of thirty substances. As is usual, each preparation has been checked independently, and thus one may confidently expect to be able to repeat the results. No change has been made in the mode of presentation.

The substances whose preparations are given in this volume are of more than usual interest; many of them are substances of practical value, whilst the methods used for others are distinctly worthy of study. Among the former class may be mentioned diazomethane, anhydrous hydrogen bromide and dimedone, oleyl alcohol, and among the latter nitrosomethyl urea, *p*-iodophenol, and α-tetralone.

In connection with dimedone—the modern reagent for the detection of aldehydes—it is stated that the product obtained melts at 147° C., whilst in the literature 150° C. is given. In view of this statement, it is curious that no reference is made to the work of the late A. W. Crossley on the preparation of this substance. His method, which employs the same reagents, differs only in detail from that given; but a sample of dimedone made under his direction some 15 years ago still melts at 150° C. (A recently-purchased A.R. sample melted at 147° C., and the formaldehyde condensation products from the two sources also differ slightly in melting-point.)

The volume ends with an appendix containing additions and corrections to work set out in previous publications, and a subject index covering Volumes X to XV. Volume XV being well up to the standard of its predecessors, and also more than usually interesting, may be recommended to all interested in the preparation of organic chemicals.

HAROLD TOMS

EINFÜHRUNG IN DIE ORGANISCH-CHEMISCHE LABORATORIUMSTECHNIK. By Dr. KONRAD BERNHAUER. Pp. x + 129. Berlin: Julius Springer. 1934.

This little book, which is very clearly printed in Roman type, is, as its title suggests, an introduction to the laboratory technique of organic chemistry. It is suitable for advanced students and those beginning any form of research needing skill in the manipulation of the apparatus used in the preparation of organic substances. It thus occupies a place between the ordinary text-books of practical organic chemistry and the great reference works.

The subject is not developed in historical order, for this, as is implied in the preface, would have necessitated the inclusion of methods which, although useful in their day, have long since given place to better ones, and the author's endeavour has been to include only methods which are well-tried and tested. Numerous items of sound advice are given to the worker; thus, he is urged to acquire a thorough familiarity with vacuum work in all its aspects.

After a general introduction, dealing with organic reactions and the isolation, purification and characterisation of organic substances, there follow very detailed sections on almost every operation and variation thereof likely to occur in the organic laboratory. In brief, the principal subjects dealt with are:—Section I, general matters concerning heating, cooling and vacuum apparatus; Section II, methods for carrying out reactions classified according to the type of apparatus needed; Section III (which constitutes the major portion of the book) describes methods for isolating and purifying substances, and gives valuable detail of such processes as distillation, evaporation, sublimation, extraction, crystallisation and absorption. The appendices deal with: (i) Glass apparatus; (ii) the handling of corrosive, poisonous and explosive materials; and (iii) the organisation of laboratory work. Lastly, there are some very noteworthy remarks on the art of writing for publication. A comprehensive index is also included.

Dr. Bernhauer's book is a very satisfactory volume. It is up-to-date, for it contains references to 1934 publications and includes an account of the application of adsorption methods for the purification and separation of compounds of definite structure (such as the carotenes) and of enzymes. Micro- and semi-micro methods also receive attention. The book is clearly printed, contains many excellent diagrams and much useful information and is essentially a work for the laboratory and is well worthy of attention. HAROLD TOMS

PLANT PHYSIOLOGY. By MEIRION THOMAS, M.A. Pp. xii + 494; with 75 illustrations. London: J. & A. Churchill, Ltd. 1935. Price 15s.

In the preface the author says "It is true that excellent recent and older works exist, but they are not numerous, and there is still room for several more in which the subject is treated from different standpoints and with different objects in view." He then explains that the present book has been written to assist students who wish to develop the knowledge of plant physiology that they have acquired in general courses on botany, and it is hoped that it will prove useful to students of chemistry, physics, agriculture, and other subjects, as well as to students who are making a special study of botany. It may be said at once that in the reviewer's opinion this book should go a long way towards achieving the author's purpose. To produce a concise and readable account of plant physiology within the limits allotted is no mean achievement, and great credit is due to the author for the way in which he has selected his material so as to present a reasonably complete picture of present-day knowledge of the subject.

The book is divided into four parts and two appendices: Part I, entitled Protoplasm, consists of three chapters dealing with the living cell as a whole, the physico-chemical heterogeneity of protoplasm, and protoplasm as a chemically active system. Part II deals in ten chapters with the absorption, translocation and elimination of water solutes and gases, with special reference to the physical and chemical principles underlying these phenomena. Part III consists of four chapters concerned with metabolism, photosynthesis and respiration. Part IV is devoted to growth and movement, and contains a commendably lucid and up-to-date account of recent work on hormones. Appendix I gives a brief account of the chemistry of all the more important metabolic products occurring in plants, and Appendix II deals with aspects of physical chemistry. A minor blemish, which, none the less, calls for comment, is the peculiar misprint on page 419 of *Isatia tinctora* for *Isatis tinctoria.*

The book may be confidently recommended as a handy and reliable source of information on the subjects with which it deals. P. HAAS

QUALITATIVE CHEMICAL ANALYSIS. By F. MOLLWO PERKIN. Fifth Edition, revised by Dr. J. GRANT. Pp. viii + 377. London: Longmans, Green & Co., Ltd. 1935. Price 9s. net.

In this new edition Dr. Grant has preserved the general outlines of the original issue, while bringing the subject-matter thoroughly up to date. The classical methods of separation are retained, but the use of modern reagents is fully described wherever applicable—usually in the form of confirmatory tests; for example, the specific organic precipitation reagents for metals. The use of micro-analytical methods is encouraged, and a surprisingly comprehensive series of micro-tests, requiring the simplest of apparatus, is given. The "rarer elements" are adequately dealt with, methods of identification being described under the appropriate group separations.

The organic sections have been amplified to some extent, particularly that on the alkaloids. With reference to the determination of melting-points, the corroborative "mixed melting-point" test might usefully have been mentioned.

Few errors are to be noticed in the text; in paragraph 7 on p. 146, "test for iodine" should read "test for iodide"; on page 227, thiosulphuric acid is mentioned where thiocyanic acid is meant.

In the separation of metals by hydrogen sulphide, students are warned of the tendency of the sulphides of tin and cadmium to be held up by strong hydrochloric acid; the warning might well have been extended to include lead sulphide, precipitation of which is prevented by as little as 3 per cent. of hydrochloric acid. A curious error has crept in on p. 171 concerning the separation of sulphur acids, confusion having arisen from the replacement of $PbCO_3$ in the earlier edition by

$CdCO_3$ in the present issue. In describing the well-known turmeric reaction with boric acid, no mention is made of the necessity to dry the test paper subsequently. These, however, are minor matters, and do not detract from the general excellence of this revision of a deservedly popular text-book. J. U. LEWIN

INFRA-RED PHOTOGRAPHY. By S. O RAWLING, D.Sc., F.I.C. Second Edition. Pp. xii + 66. London and Glasgow: Blackie & Son, Ltd. 1935. Price 3s. 6d. net.

It is not surprising that there has been an early demand for a new edition of Dr. Rawling's compact little guide to infra-red photography, for it happily combines theory with practice in a way that makes an appeal both to the scientific worker and to the amateur photographer.

The general arrangement of the book is the same as in the previous edition, but there is a considerable amount of new matter embodying the results of work done during the past two years. There are now also numerous references to scientific journals and a useful bibliography of papers relating to infra-red sensitising dyes, but there are still many gaps. For instance, there is no mention of Plotnikow's discovery of longitudinal striation and reflex scattering of rays, which affords the best, if not the only satisfactory, explanation of such infra-red phenomena as the resistance of the eye to the heat rays of a tropical sun.

The praise that was given to the first edition (ANALYST, 1933, 58, 726) may be extended to its successor. Infra-red photography is relatively so simple in technique, and has so firmly established its value in scientific work, that it must be increasingly used in future. Anyone with an elementary knowledge of ordinary photography will find in this book the way of dealing with any difficulties he may encounter when first he attempts to apply his methods in a region beyond the visible spectrum. EDITOR

DECEMBER, 1935 Vol. 60, No. 717

4. JAN. 1936 INST. AGR. RES.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, November 6th, the President, Mr. John Evans, M.Sc., F.I.C., being in the chair.

Certificates were read in favour of Kenneth Franklyn Allen, B.Sc., Vincent Anthony Cachia, B.Sc., A.I.C., Alfred Randolph Campbell, F.I.C., Philip Farrugia, B.Sc., M.D., George Eric Forstner, M.Sc., A.I.C., Harry Richard Knight, A.I.C., A.R.S.M., William George Mitchell, Theodore Lawrence Parkinson, B.Sc., A.I.C., Herbert Stanley Redgrove, B.Sc., F.I.C., Herbert Newton Wilson, F.I.C., William Wilson, F.I.C.

The following were elected Members of the Society:—William Reginald Bage, Albert R. Bonham, B.A.Sc., F.C.I.C., Henri Charles Philip Chapleau, B.A.Sc., Leo Cooksey, B.Sc., F.I.C., Douglas Eric Davis, B.Sc., F.I.C., Frederick Ellington, B.Sc., A.R.C.S., A.I.C., Edward Oscar Heinrich, B.S., James Arthur Durham Hickson, B.Sc., A.I.C., Donald Robert Jackson, Daniel Carswell Macpherson, B.Sc., Florence Ellen Murphy, B.Sc., Temple Clifford John Ovenston, B.Sc., Ph.D., A.I.C., George Herbert Stott, M.Sc., F.I.C., Basil C. L. Summers, B.Sc., Stanley Gordon Willimott, B.Sc., Ph.D., A.I.C.

The following papers were read and discussed:—"Characteristics of Halibut Liver Oils," by R. T. M. Haines, M.A., and J. C. Drummond, D.Sc., F.I.C.; "Notes on Mendel and Goldschieder's Method for Determining Lactic Acid in Blood," by R. Milton, B.Sc.; "The Application of Controlled Potential to Microchemical Analysis," by A. J. Lindsey, M.Sc., A.I.C., and H. J. S. Sand, D.Sc., Ph.D., F.I.C.; and "The Micro-Electrolytic Determination of Bismuth and Lead and their Separation by Graded Potential," by A. J. Lindsey, M.Sc., A.I.C.

SCOTTISH SECTION

The opening meeting of the Section was held in Glasgow on November 13th, 1935, Mr. R. T. Thomson, F.I.C., being in the chair. Dr. T. W. Drinkwater, Vice-Chairman of the Section, was unable to be present owing to illness. Sixteen members attended.

The Section was honoured by the presence of Mr. John Evans, M.Sc., F.I.C., President of the Society; Dr. G. Roche Lynch, Hon. Secretary; Dr. E. B.

Hughes, Hon. Treasurer; and Professor W. H. Roberts, Chairman of the North of England Section.

Apologies for absence were intimated from Dr. C. Ainsworth Mitchell, Dr. T. W. Drinkwater, Mr. T. Cockburn and Professor J. Hendrick.

The following papers were read and discussed:—"Some Properties of Sodium Hexametaphosphate," by R. T. Thomson, F.I.C.; and "The Determination of Iodine in Kelp," by J. B. McKean, F.I.C.

Obituary

SAMUEL FRANCIS BURFORD

On 29th August Samuel Burford passed away at the home of his son at Rickmansworth. He had reached the good age of 78 years, and his death deprives the Society of another old and very loyal member.

Originally intended for the printing trade, Burford early interested himself in pharmacy, and passed the Major Examination of the Pharmaceutical Society in 1883. He subsequently continued the study of analytical chemistry under Dr. John Muter in London. In 1892 he started a practice as an analytical and consulting chemist in Leicester, and in the same year joined the Society of Public Analysts, being elected a Vice-President in 1924–1925. He was also for many years a member of the Chemical Society, and in 1918 was elected a Fellow of the Institute of Chemistry.

As part of his practice, he acted as chemist to the Corporation sewage, water and other departments, and in 1913 was appointed Public Analyst for Leicester. The post was originally a part-time one, but was constituted a whole-time appointment in 1925 on the construction of the City Laboratory. He retired from practice in 1929.

In the course of a busy career Burford found time for many activities outside his profession. He was recently President of the Leicester and Leicestershire Chemists' Association for two or three years, a position he gave up only from ill-health just before his death. He had also been a member of the Highfields Hospital Committee since its foundation, and Honorary Secretary since 1918.

He was well known in Free Church circles, and had been on the executive of the Leicester Free Church Council for many years. At one time a lay preacher, he was always an active worker in his own circle, and his services could always be relied upon for a worthy cause. He took an active part in adult school work, and was recently elected President of the Leicestershire and Rutland Band of Hope Union after having been a vice-president for many years.

His character was one of great kindliness; his simplicity of manner and evident honesty of purpose endeared him to those about him. A life-long abstainer and non-smoker, he was yet blessed with a spirit of tolerance and a keen sense of humour that made him very human.

He outlived his wife by less than a month, and leaves a son, a daughter and two grandchildren, to all of whom the sympathy of the Society is extended. At his funeral the Society was represented by the writer. F. C. Bullock

The Chemical Examination of Furs in Relation to Dermatitis

Part VI. The Identification of Vegetable and Other Dyes

By H. E. COX, D.Sc., Ph.D., F.I.C.

(*Read at the Meeting, October* 2, 1935)

An experience ranging over several hundred cases of alleged fur dermatitis shows that this disease rarely arises from the common vegetable dyestuffs used on fur. It is true that a few such cases have been recorded, but in some of these it may be doubted whether the real identity of the irritant substances was adequately determined; for it is desirable to find out not only what is present but also what is absent. I have shown in an earlier paper[1] that in the great majority of cases the nocuous substance has been found to be an amino compound in an unoxidised or partly oxidised state. In order to get any understanding of the physiological causes of skin irritation in connection with dyes it is essential to accumulate accurate data as to the constitution of substances which are irritant and those which are not; this pre-supposes analytical diagnosis of the pigment and proof that the particular dyestuff, and no other, is present. The analytical recognition of fur dyes—or hair dyes—is often a difficult matter. Complications are caused by the fact that in any given case there may be two vegetable dyes with or without an oxidation dye, and the reactions of the vegetable dyes are complicated by the presence of the mordant and of various tannins and other substances which may be extracted from the fur fibres. Occasionally, mineral pigments are used.

The number of vegetable dyes known to be used on furs is not very large, but by the skilful use of mordants a wide range of colours is obtainable. Besides those used on fur, there are a few others used as hair dyes which I have included in this section; there is no real difference between a hair dye and a fur dye, and it is common to both that they must be applied at quite low temperatures and without strong acid or alkali. The number of possible oxidation dyes is legion. It is true that about a dozen are in common use, but some hundreds have been described or patented in recent years, and it is impracticable to devise a scheme which would cover all the possibilities. It is proposed to describe the chemical nature and reactions of the principal vegetable dyes which are met in practice and a scheme of analysis which will often suffice to discover with what substance or substances fur or hair has been dyed. It should be clearly stated that no scheme can cover all types, and that more than one substance may be met in any given case. The topping of vegetable colours with an oxidation colour is common practice, either for improving the shade or lustre of a fur or for levelling up the colour of a composite garment. There are reasons for thinking that in some of the reported cases of vegetable dyes an oxidation dye was really present as a "topping." The very common case of diamines on logwood has been considered in Part V of this series.[8]

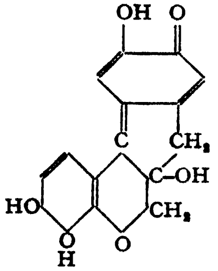
SOME PROPERTIES OF UNDYED FUR.—Undyed fur as it appears in commerce is peculiarly resistant to chemical agents. Three factors seem to contribute to this: one, the high resistance of the keratinoid fibres in which the pigment is encased; two, the nature of the pigment itself, about which so little is known; and three, the processes of curing which the pelt has undergone at the hands of the fur dresser. Animal hair is, in general, coarser and more resistant to bleaching agents than is human hair, which, as everyone knows, is easily bleached by peroxide. Furs are slowly bleached in acid solution by sulphur dioxide, but they yield more readily to oxidising agents such as permanganate, hypochlorite or hydrogen peroxide in weak alkaline solution. In dyed furs the dye is largely on, or near, the surface of the fibres, so that it is more quickly bleached than the natural colours, which are mainly inside the fibre. The nature of the pigment in animal or human hair is unknown; possibly it varies in different species. It is generally fat-soluble, and is thought to be an oxidation product of amino-compounds such as tyrosine, effected by tyrosinase or other natural enzymes. Microscopic examination shows that the pigment is distributed in granules in the medulla; the size and frequency of the granules are influenced by climate, season and food, as well as by the species of animal. These colour granules gradually diffuse outward into the fibre itself, but even there they are protected by the keratin and the film of oil, which prevent the penetration of watery reagents unless an alkali is added. It is well known in the trade that the hair of animals from wet districts contains more pigment than that of the same species in dry places. The lipoid nature of the pigment appears to be related to the water-resisting properties of the fur. Also, the process of rolling or calendering, commonly employed to give lustre, makes the fur more resistant. When fur has been dyed by a dipping method the pelt is stained, and inspection discloses the fact; this simple observation of course fails to reveal evidence of the common process of brush dyeing.

As an alkaline solution of hydrogen peroxide ultimately destroys the colour both of dyed and undyed fur, it is not really useful as a reagent for testing purposes. Sodium formaldehyde sulphoxylate ($NaHSO_2.HCHO.2H_2O$), however, reduces most artificial dyes quickly, but does not markedly bleach an undyed fur in a short time; it is therefore quite useful as a differential reagent. Hot dilute hydrochloric acid has very little action on the colour of natural hair; the fibre is, of course, weakened, and various nitrogenous substances, with little of the vegetable pigment, are extracted. On the other hand, nearly all the artificial pigments are either extracted or decomposed by such treatment, so that one gets a solution of the dye, complicated, of course, by the presence of tannins and keratin products.

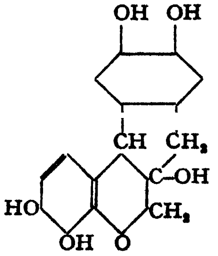
Heavy or dark dyeings are easily recognised, but the lighter shades, tinting and topping, often present difficulties.

VEGETABLE DYES COMMONLY USED ON FURS.—It is necessary to consider in detail the nature and chemical constitution of the substances used as dyes, not only for the sake of finding their reactions, but for the more important object of considering their possible action on the skin, and in what way they differ from dyes or intermediates known to be irritant. The following vegetable substances are common on furs: logwood (including brazil wood), quercitrin (black oak), flavin, fustic, catechu and similar tannins, gall-nuts, occasionally turmeric, and, for hair, henna. Each of these substances may be combined with iron, copper, chromium, aluminium or other metal as mordant, and the shade of the dyed fur is dependent as much on the mordant as on the dyestuff. Hence the ash of the hair should be examined for metals, in view of the fact that iron will always be found and traces of other metals may be present from natural causes. Lead, silver, mercury and bismuth are sometimes used in the form of mineral pigments.

Logwood.—This well-known dye wood has been in use in England for about 400 years,[3] though it was at one time put under a ban by Queen Elizabeth. This ban had nothing to do with dermatitis, but was due to the failure of the dyers of those days to use it properly so as to get good permanent results. Charles II removed the prohibition, and, since then, the dye has enjoyed a deservedly high reputation, alike for excellence of colour, permanence and harmlessness. It was included in the early editions of the London Pharmacopoeia. The colouring matter of *Haematoxylon campechianum* is haematoxylin, which is the leuco compound of the true dyestuff haematin. Brazil wood (*Caesalpinia sappan*) contains a methyl ether of haematoxylin, which yields this substance on oxidation. It has been shown by the work of Perkin, Robinson[4] and others that haematoxylin and haematin contain a di-hydro-pyran group, and have the structures:



Haematin

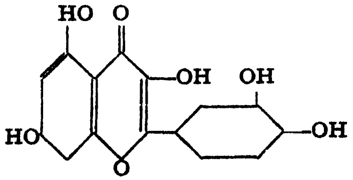


Haematoxylin

These compounds, and also brazilein, are converted into red salts when boiled with mineral acid, and their original colour cannot readily be restored. The red colour is slowly reduced by hydrogen. Sulphur dioxide forms a colourless compound by addition, not by reduction. Alkalis give a crimson colour with brazil wood, violet with logwood; ferric chloride gives deep brown or purple-black, and lead acetate a pink or blue precipitate, respectively. The red colour is destroyed by reduction with zinc or tin in acid solution, and is restored by exposure to the air; the reduced solution gives no indamine reaction and no diazo compound. These facts are useful in a search for admixed oxidation colours. Alum gives a rose-red lake, and pyrogallol, for which a delicate test is available, may be formed by fusion with alkali.

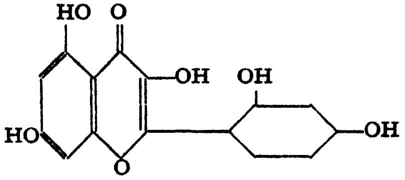
Logwood is usually met with in dark brown or black dyed furs mordanted with copper or iron, and may be stripped by boiling with dilute hydrochloric acid.

Quercitrin is another wood dye whose history goes back about 250 years. The dye is obtained from black oak, in which it occurs as the glucoside, quercitrin, which, on hydrolysis, yields the flavone dye, quercetin, having the constitution (Perkin[5]):



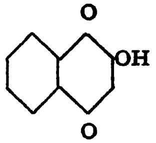
Flavin is a commercial preparation of quercitrin and yields stronger colours than does the bark itself. It dyes fur brown with chromium, orange with aluminium, yellow with tin, and olive with iron as mordant. Quercitrin gives a yellow precipitate with lead acetate. It should be noted that the OH groups in the flavone ring are at the 3′, 4′ positions; Robinson has shown that addition of ferric chloride to an alcoholic solution of anthocyanins or anthocyanidins containing OH groups in these positions gives a blue colour, becoming violet on the addition of water. Dilute aqueous solutions give no diazo reaction, but a slight brown indamine colour.

Fustic (old fustic), the wood of *Chlorophora tinctoria*, contains another flavonol derivative, morin, which is closely allied to quercetin. Kostanecki and others[6] give it the structure:



It dyes furs thus:—With chromium, olive yellow; aluminium, yellow; tin, yellow; iron, deep brown; it is much used in conjunction with other colours to produce brown and drab shades. In solution it forms an orange precipitate with lead acetate and an olive green with ferric chloride; with nitrite it gives a dark colour intensified by alkali, and with diazobenzene chloride a yellow dye. The indamine reaction is negative. Fusion with alkali yields both phloroglucinol and resorcinol.

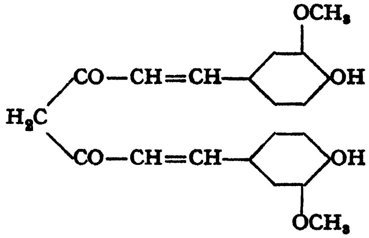
Henna.—This well-known hair dye is used but seldom on furs, though its use for hair and nails dates back to the days of the Pharaohs, a time, we are told, when dyed finger and toe nails were not confined to the young and fashionable, but were common to all women. The active principle of the leaves (of *Lawsonia alba*) is lawsone, which is probably identical with 2-hydroxy 1 : 4 naphthaquinone,[7, 8]



and has m.p. 192–195° C., though some other substances are present also. It dyes hair or wool an orange-yellow, which is intensified by ammonia, but is not very permanent. The colour is extractable from aqueous solutions by ether; if sufficient colouring matter is available, henna may be recognised by the strong absorption band of an amyl alcohol extract at 656–670$m\mu$. When considering its chemical reactions it should be remembered that commercial henna powders frequently contain pyrogallol, and often a metallic salt or even an amino compound. An alcoholic solution gives a red colour with nickel acetate, or an orange colour with copper acetate. Aqueous solutions show:

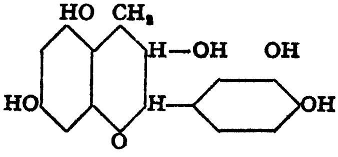
With ferric chloride — a greenish liquid which should not give a black colour when poured into excess of dilute ammonia (absence of pyrogallol).
Indamine test — negative.
Sodium nitrite — no colour.
Diazobenzene — a red colour or precipitate, yellow if very dilute.
Heated with zinc dust — no red colour.

Turmeric, the rhizome of *Curcuma longa*, affords another well-known yellow pigment, curcumin, which is much used in India and a little in England as a hair dye, rather than for furs. It is employed sometimes as a direct dye, but more usually with a mordant in place of fustic. The colour is not resistant to light or alkalis. With chromium, the colour is brown; aluminium, yellow; tin, orange; and iron, a brownish-black. The structure of the dye, according to Kostanecki[9] and Rupe,[10] is:



When the dye is dissolved in concentrated sulphuric acid the colour is bright red, a fact which provides a direct test on hair or fur. Lead acetate gives a yellowish precipitate. The familiar reaction with boric acid in acid solution is due to the formation of rosocyanin, which is isomeric with curcumin and forms characteristic blue-green salts with potash or ammonia. Turmeric gives but little colour with ferric chloride, is not diazotised by nitrite, and forms no indamine. Alcoholic or ethereal extracts show a green fluorescence.

Catechu, or cutch, is much used for some types of fur. The colouring matter, catechin, belongs to the coumarone group, and exists in dextro and laevo forms. According to Mason,[11] the *d*-variety has the structure



Mordanted with iron, fur is dyed a brown-olive colour. The solution gives a deep green colour with ferric chloride, a white precipitate with lead acetate, and, when oxidised with dilute ferricyanide in presence of potassium acetate, an orange precipitate. On addition of concentrated sulphuric acid to a hot acetic acid solution of catechin, an orange-red powder—the characteristic phlobaphen—separates. Mitchell's ferrous tartrate reagent gives no characteristic colour, but hydrochloric acid and sodium nitrite give a dark brown, and the product, like that of some other tannins, coupled with alkaline β-naphthol, is deep red. There is no indamine reaction—other than the ferric chloride colour. A match-stick with hydrochloric acid gives the phloroglucinol colour.

Gall Nuts and Oak-bark.—The various forms of gallotannic or quercitannic acid are much used on certain types of grey fur, such as squirrel or moleskin. These, and some other tannins, cannot usually be separately identified on the fur. A well-known black is produced from gall nuts and sumach mordanted with sulphate of iron and copper in the presence of litharge and alum. These tannins give marked colours with Mitchell's ferrous tartrate reagent. Ferric chloride shows a brownish-green with quercitannic acid and blue-black with gallotannins. The indamine reaction is negative, but nitrite gives a brown colour which is intensified when coupled with alkaline β-naphthol. Bromine produces a yellowish-white precipitate.

Pyrogallol, obtained from gallic acid, is also much used on grey furs, such as squirrel. Some of its reactions in dilute solution have been given in an earlier paper of this series.

Further details of the many identification reactions of the tannins are given in Vol. V of *Allen's Commercial Organic Analysis*, so that it is unnecessary to amplify them here.

It will be noticed that all the foregoing natural pigments, though of varying types, have it in common that they are non-nitrogenous, whereas the usual oxidation bases all depend upon nitrogen groups for their activity. Most of the textile dyes which arise in this connection are likewise nitrogenous. The analysis of dyed furs is complicated by the fact that some nitrogen is always extracted by water or solvents, and that many of the tannins (which are so commonly present) give coloured oxidation products, react with sodium nitrite, and, when coupled with alkaline naphthol sulphonic acids, give colours simulating the diazo reaction. Also, some tannins give a pseudo-indamine reaction, so that a green indamine must not be taken as necessarily indicating a diamine.

The following tables show a simple, but not exhaustive, scheme which will usually indicate the nature of any artificial dyestuff present on a fur. The tests are conveniently applied in ordinary test-tubes to small clippings of the hair.

TABLE A

Boil the fur fibre with dilute hydrochloric acid (1:10)

Fur unaffected; liquor not coloured	Fur reddened; liquor bright red	Fur partly bleached; liquor not coloured	Fur not much changed		
			Liquor dark brown	Liquor yellow	Liquor greenish
1	2	3	4	5	6
Undyed fur	Logwood Brazil wood and some oxidation colours	Metallic pigments: Lead Silver Bismuth	Oxidation colours: Aniline black. Also cutch with Cu or Cr	Turmeric Henna Fustic Quercitrin	Tannins Oak-bark Gall nuts. Liquor nearly colourless: Pyrogallol

They should be applied to several pieces taken from any differently coloured parts; the leather should not be included, or misleading results are likely to be obtained from the various leather extractives.[12] The method follows the plan adopted by A. G. Green in his work on *Analysis of Dyestuffs*, which is so useful for the identification of the older types of textile colours.

TABLE B

Boil for half a minute with sodium formaldehyde-sulphoxylate solution*

The fibre is unaffected	Fibre slightly bleached	Fibre much bleached		
1	2	3. Oxidation colours from amines, etc. Turmeric, henna Many textile dyes, such as:		
Undyed fur Aniline black Cutch is almost unaffected	Fustic Quercitrin Flavine Tannins			
		4	5	6
		Azines. Colour restored on exposure to air	Triphenylmethane colours. Restored by persulphate	Nitro and azo colours. Not restored by air or persulphate

* This solution is prepared according to the formula of A. G. Green:—Dissolve 50 g. of sodium formaldehyde-sulphoxylate in 150 ml. of hot water; grind 0·25 g. of precipitated anthraquinone into a paste with some of this solution, then dilute the whole to 500 ml. The solution should be practically neutral, not acid.

Notes.—A (1). Observe if the pelt is unstained.

A (2). The acid extract from logwood and the other red woods gives characteristic blue or violet colours with alum and ammonia, whereas oxidation colours give only brown or black. Make the acid extract nearly neutral with chalk, add a little zinc dust, and filter; then apply the indamine reaction. The resulting colour varies somewhat with the concentration, but may be:

TABLE A (2)

Blue-green	Brown-pink	
p-Phenylenediamine *p*-Tolylenediamine *p*.*p*′-Diamino-diphenylamine, etc.	Meta-diamines *o*-Amino-phenol *m*-Amino-phenol, etc.	*p*-Amino phenol 2:4-Diamino-phenol Dimethyl-*p*-phenylenediamine *p*-Aminodiphenylamine, etc.

A (3). Lead sulphide, mercury sulphide, silver or bismuth compounds may be detected here; identify in the ordinary way.

A (4). Test for oxidation colours as in A (2). Cutch gives a dirty green colour with ferric chloride, and gives the diazo reaction; confirm by the reactions given on p. 797.

A (5). The colour will be darkened on adding ammonia; recognised by the boric acid reaction. Henna can be identified by the red colour it gives in alcoholic solution with nickel acetate. Fustic is indicated by the formation of a yellow dye with diazobenzene, and of an orange precipitate with lead acetate in neutral solution. Quercitrin gives a negative diazo reaction and the other tests as shown on p. 796.

A (6). Make the solution nearly neutral and add

(*a*) One per cent. iron alum solution; a purple or black colour indicates a catechol tannin.

(*b*) Mitchell's ferrous tartrate reagent: gallotannins (and a few anthocyanins) give a blue-black colour; ellagitannins show only a dirty green.

(*c*) Ferric chloride, and pour into excess of very dilute ammonia: pyrogallol gives a black colour.

If sufficient material is available, the goldbeaters' skin test is applied; it is specific for tannins.

B. The effect of boiling with a reducing solution, such as this, is one of degree; nearly all the furs are partially bleached on prolonged boiling, so that it is important not to continue too long. The coarser types of hair are more resistant than the small soft varieties.

B (1). Some mineral pigments, such as lead sulphide, will also be unaltered. Indications of these or of aniline black will be obtained by the acid boiling.

B (2). The resistance of these varies somewhat according to the mordant; acid treatment strips them quickly.

B (3). A mordant is usually present with the oxidation colours; the reduction process gives rise to an amine in most cases, but not always the original amine.

B (4, 5 and 6). Textile dyes, such as these, can usually be applied only at high temperatures which cannot be used with furs unless they have previously been chrome-tanned, *e.g.* some seal skins. Examine the pelt for substantial quantities of chromium. If textile dyes are present, the methods described by Green should be used.

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DISCUSSION

Mr. C. E. SAGE had hoped to hear from Dr. Cox whether there were any particular dangers attached to the use of vegetable dyes. His own experience with logwood over many years showed that it was not harmful, and the irritation it sometimes caused was only what was to be expected from the dusty particles. The pigments from some berries caused irritation between the fingers of the workpeople, and archil gave rise to complaints occasionally, but whether that was due to the pigment or to the method of its preparation, was not known.

Mr. H. S. REDGROVE said that he would like to express appreciation of Dr. Cox's paper, because his own interest centred in dyes used for living hair, and he did feel that the chemistry of hair dyes needed exploring and clearing up. He and the late Mr. Foan had made some efforts to shed light on this subject, but there was an enormous amount of work still to be done, and Dr. Cox's results, in so far as he had touched on dyes used for living hair, were exceedingly welcome. During the past few years a large number of materials for dyeing hair (about which various claims were made and of which absolutely nothing was known) had been placed on the market. The position was extremely unsatisfactory. If one wanted to colour a textile or food one could order a dye under the Colour Index number, but if one wanted to dye hair one had to order the dye under some fancy name and hope for the best. He was glad that Dr. Cox had emphasised the fact that so-called henna was usually a mixture. There was a large amount of misunderstanding about this; the hairdressers still did not know what they were getting, although for years the chemist had been trying to tell them. He expressed the hope that Dr. Cox would continue his work on the dermatological effect of dyes, particularly dyes used for hair.

Dr. Cox replied that, in his experience, dyes used on human hair sometimes produced strange effects. He agreed with Mr. Redgrove that the subject was much in need of scientific study. Permanent waving, too, was apt to modify the colour of dyed hair, and he had seen some odd results due, apparently, to chemical reactions induced by, or during, permanent waving.

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The Determination of Iodine in Iodised Salt

By R. L. ANDREW, F.I.C., and J. L. MANDENO, M.Sc.

As a result of the campaign against endemic goitre, iodised salt is widely used in New Zealand. The Regulations under the Sale of Food and Drugs Act require that it shall contain not less than 1, or more than 2 parts of potassium iodide or sodium iodide in 250,000 parts. As it is important that these limits shall be observed, iodised salt is frequently examined in the Dominion Laboratory for its iodide-content.

The analytical process employed is based on that of Winkler, in which the iodide is converted to iodate by chlorine, thus, $KI + 3Cl_2 + 3H_2O = KIO_3 + 6HCl$. After the excess of chlorine has been removed by boiling, potassium iodide is added, when $5KI + KIO_3 + 6HCl = 6KCl + 3I_2 + 3H_2O$. The liberated iodine is titrated with standard thiosulphate solution. With certain refinements, quantities of iodine as small as $0{\cdot}2\mu$ can be determined by this method, which is therefore employed in the examination of biological materials. In iodised salt the quantity of iodine to be determined is very much larger than this.

The details of the method, as recommended by von Fellenberg, are as follows:—The salt (100 g.) is dissolved in water, the solution is made up to 500 ml. and filtered, 200 ml. of the filtrate (= 40 g. of salt) are placed in an Erlenmeyer flask, and 1 ml. of chlorine water and 2 ml. of *N* hydrochloric acid are added, together with a small piece of calcite or a few fragments of pumice, to prevent bumping. The solution is boiled until salt begins to separate. Sufficient water to dissolve the separated salt is then added, and the solution is cooled. Two ml. of strong phosphoric acid are then added, followed by about 0·2 g. of potassium iodide and a few drops of dilute starch solution, and the liquid is titrated with *N*/500 thiosulphate solution.

It was found more convenient to use bromine water instead of chlorine water, and *N*/500 thiosulphate solution instead of the stronger solution. This method, as outlined, did not give quantitative results, and the proportions of iodide in samples were calculated from the results obtained under the same conditions with solutions of salt containing known amounts of added potassium iodide. On several occasions the results were anomalous, and investigation showed that increase in the acidity of the solution lessens the amount of iodide converted into iodate. If, however, water is used instead of salt solution, the conversion is practically complete over the same range of acidity. This is shown below. In series A, 0·3 mg. of potassium iodide was added to each of 8 lots of 200 ml. of salt solution. The solutions were just alkaline to methyl orange, one drop of *N* hydrochloric acid being sufficient to render them distinctly acid. Varying amounts of acid were added. In series B, 200 ml. of water were substituted for salt solution. The experiments were then carried through, as outlined above, with the following results:

	N hydrochloric acid added ml.	*N*/500 thiosulphate required A ml.	*N*/500 thiosulphate required B ml.
1	None (just alkaline)	5·3	5·2
2	0·05	5·3	5·2
3	0·5	4·8	5·2
4	1·0	4·3	5·2
5	2·0	2·8	5·2
6	4·0	1·6	5·2
7	10·0	0·6	5·2
8	20·0	0·4	5·2

If a complete conversion took place, 5·4 ml. of *N*/500 thiosulphate solution would be required for the titration. It will be seen that in B, when water was used, almost quantitative results were obtained over the whole range, but that with the salt solution there was a distinct falling off with as little as 0·5 ml. of *N* hydrochloric acid, and with 2·0 ml. (the amount recommended by von Fellenberg) the result obtained was little more than half the theoretical. It, therefore, appears possible that the method was originally worked out by using water instead of a salt solution. In the numerous references in the literature stress is not laid upon the importance of working near the neutral point; some say, make faintly acid, some just acid, and others distinctly acid. It was found that there was no advantage in adding phosphoric, instead of hydrochloric, acid to the solution before titration. Finally, the method was modified by making the salt solution just acid to methyl orange before adding the bromine water, and adding 2 ml. of *N* hydrochloric acid before titrating with *N*/500 thiosulphate solution. Numerous experiments with salt solutions containing a wide range of known added amounts of potassium iodide have shown that the process so modified is practically quantitative over any range of values likely to be met with in practice.

The apparent loss of iodine when the process is carried out in increasingly acid solutions is of some interest. If the reaction $KI + 3Br_2 + 3H_2O = KIO_3 + 6HBr$ is the only one proceeding, and is reversible in acid solution of sodium chloride, the whole of the iodide will be present at the end of the reaction as a mixture of iodide and iodate, the proportion of each depending on the acidity of the solution. To test this, a series of experiments was carried out as in series A, down to the separation of salt; the solutions were cooled, diluted to the original volume, neutralised with *N* sodium hydroxide solution, and made just acid to methyl orange, bromine water was added, and the experiments were carried through to titration with *N*/500 thiosulphate solution. The results obtained are given under C.

N hydrochloric acid added ml.	*N*/500 thiosulphate solution required C ml.	A (for comparison) ml.
0·05	5·3	5·3
0·50	5·3	4·8
1·0	5·2	4·3
2·0	4·8	2·8
5·0	4·4	1·6
10·0	3·8	0·6
20·0	2·8	0·4

It was shown (see above under A) that near the neutral point the conversion of iodide into iodate is quantitative. If no iodine were lost from the solutions with increasing acidity, all the quantities under C would therefore be 5·3 ml. of *N*/500 thiosulphate solution. It will be seen that, with 20·0 ml. of added *N* hydrochloric acid, iodide equivalent to 2·5 ml. of *N*/500 thiosulphate has been lost from the solution, while the equivalent of 2·4 ml. has undergone reversion from iodate to iodide. In other words, with increasing acidity the conversion of iodide into iodate in presence of sodium chloride is progressively less complete, and at the same time increasing amounts of iodine (possibly as monochloride) are lost from the solution.

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WELLINGTON, NEW ZEALAND

A Contribution to the Iodimetric Titration of Tin

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IN the iodimetric titration of tin a hydrochloric acid solution of the metal is first reduced to the stannous condition. A number of reducing agents have been recommended for this purpose; metals such as iron, aluminium, nickel, zinc and lead have generally been used; more recently, hypophosphorous acid has been advocated.[1]

The stannous chloride so obtained is titrated against a solution of iodine in aqueous potassium iodide solution, precautions being taken to prevent oxidation by air during the titration.

The reaction is given by the equation:

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI,$$
$$\text{or } Sn^{++} + I_2 = Sn^{++++} + 2I^-.$$

The first method for attaining accuracy was suggested by Lenssen,[2] who carried out the titration in an alkaline tartrate solution and reported good results by iodine titration. Benas[3] found that inaccurate results were obtained in both acid and neutral solutions. He showed that the low results were due to the action of oxygen from the air, and that it was necessary to exclude air from the solution during titration, and proposed the addition of excess of iodine to the acid solution of stannous chloride, followed by titration back with thiosulphate. Young[4] obtained good results in acid solution, but his method of standardising the iodine solution against potassium dichromate by titration of stannous chloride against both these oxidising agents consists, in effect, in standardising the iodine against stannous chloride, so that his results do not prove that he had eliminated the oxygen effect. Borgman[5] found that the reaction between stannous chloride and oxygen is catalysed by potassium iodide; he, therefore, suggested the use of an alcoholic iodine solution, with cacothelin, instead of starch, as indicator. Kolthoff[6] found that Borgman's method gave results which were still somewhat too low. He noticed that the presence of a small quantity of antimony decreased the oxidation by air, and proposed its addition as an anti-catalyst; but, as the stannous chloride and oxygen reaction was not entirely suppressed in a direct iodine titration, he finished the determination by addition of excess of iodine, followed by titration against thiosulphate. Köhler[7] added to the stannous chloride solution excess of iodine dissolved in potassium thiocyanate, and then titrated back with thiosulphate. Jilek[8] obtained correct tin titrations by keeping the solution strongly acid, adding excess of iodine and titrating back with thiosulphate. Höltje,[9] for the determination of about 1 mg. of tin, added excess of dilute iodine solution containing only two to three g. of potassium iodide per l., and titrated the excess with thiosulphate.

The investigators so far mentioned used various metals to reduce the tin to the stannous condition. Evans (*lóc. cit.*)[1] proposed the use of sodium hypophosphite for this purpose. Before titrating, citric acid was added, and the solution was diluted to reduce the acidity. The titration was performed in a special apparatus to secure complete exclusion of air. With pure tin solutions stoichiometric results were obtained.

Even if rigidly excluded from the stannous chloride, air is dissolved in appreciable amount in the iodine solution. This source of error has not been mentioned by any of the above workers except Köhler, who drew attention to it in the titration of tin by potassium dichromate. He expressed the opinion that in practice it is difficult to prepare and preserve air-free standard solutions.

Ramsay and Blann,[10] recognising that oxygen dissolved in the iodine solution exerted a considerable effect on tin titrations, circumvented the interference by using potassium iodate instead of iodine. The small amount of iodide produced by reduction of the iodate is not sufficient to catalyse the reaction between stannous chloride and oxygen, if the acid concentration is kept fairly low.

The position may be summarised by saying that the reaction between stannous chloride and oxygen is catalysed by both hydrochloric acid and potassium iodide; or, more correctly, by hydrogen ion and by iodide ion.

The measures which have been proposed to prevent the interference of oxygen with a tin titration may be classified under the following headings:

(i) Reducing the acid concentration; (ii) reducing the iodide concentration; (iii) adding a negative catalyst; (iv) completely preventing atmospheric air from entering the titration flask; (v) adding excess of iodine and back-titrating.

The various methods recommended for tin titrations consist essentially of combinations embodying two or more of the above precautions. Köhler (*loc. cit.*)[7] considered the preparation of an air-free standard iodine solution to be, in practice, a matter of difficulty. It would appear that most workers have overlooked the fact that the amount of oxygen present in the iodine solution is sufficient to affect a titration; or, if not, have considered that no error is introduced when the iodine solution is standardised against tin.

With regard to the above points, it may be shown that:

(1) The preparation of air-free iodine solution is attended by no great experimental difficulty.

(2) The air dissolved in *N*/10 iodine solution can account for an error of about 1 per cent., in *N*/100 solution for an error of about 10 per cent.

(3) The oxygen does not react to the same extent in pure tin solution and in solutions containing other chlorides.

The extent and variability of the error that can be caused by the oxygen dissolved in the iodine solution are illustrated by the following figures. Tin (0·1 g.) was titrated with iodine solution of various strengths, but in all cases *N*/5 with respect to potassium iodide.

TABLE I

Titrations

Strength of iodine solution	Theoretical: From wt. of I_2 ml.	Theoretical: Calc. from As_2O_3 ml.	Actual ml.	Error low ml.	Error low Per Cent.
N/5	8·42	8·42	8·41	0·01	0·1
N/10	16·85	—	16·81	0·04	0·2
N/20	33·70	—	33·28	0·42	1·3
N/40	67·40	67·40	65·04	2·36	3·6

These results supply an explanation of the well-known objection of tin assayers to working with dilute iodine solutions.

The following table shows the results obtained with two *N*/100 iodine solutions made up (*a*) with ordinary distilled water, and (*b*) with air-free water. Both solutions were *N*/5 with respect to potassium iodide.

TABLE II

Tin taken g.	Tin found: (*a*) Ordinary iodine solution g.	Tin found: (*b*) Air-free iodine solution g.
0·0119	0·0108	0·0118
		0·0118
		0·0119

The results in Table II clearly demonstrate the large error introduced by the presence of dissolved oxygen in the iodine solution. It is this error that causes low results in tin assays when the iodine is standardised against arsenious oxide or by some other method that gives a stoichiometric result. The relative error thus produced is greater the more dilute the iodine solution.

If dissolved oxygen reacted quantitatively with stannous chloride, it would correspond with a definite increase in the oxidising power of the standard solution. Correct and consistent results should, therefore, be obtained, even in dilute solutions, provided tin was used for standardising the iodine. We find, however, that, despite such ideal conditions, the results are erratic.

The reaction is also influenced by other constituents of the assay solution. The positive catalytic effect of potassium iodide, and the negative catalytic effect of antimony chloride, have already been pointed out. When dealing with pure tin solutions, the effect of the dissolved oxygen can, it is true, be kept fairly constant by performing all titrations under the same conditions. When, however, the titration takes place in the assay solution prepared from a tin ore, the position is further complicated.

The element mainly responsible for this variation of the oxygen effect is titanium, a metal commonly associated with tin minerals. Under the conditions of a tin assay it is present in the assay solution as titanous chloride. Titanous salts are strong reducing agents, but the speed of reaction of an acid solution of titanous chloride with a solution of iodine in potassium iodide is too slow to affect a titration (Yost and Zabaro[11]).

It has been found, however, that the presence of titanium causes an appreciable increase in a tin assay. This effect is not proportional to the amount of titanium present, and has hitherto remained unexplained.

In Table III are shown the results obtained when titanous chloride is added to a tin assay. The iodine solution, of approximately *N*/100 strength and *N*/5 with respect to potassium iodide, was prepared from the laboratory supply of distilled water. It was standardised against tin and its strength found to be 0·01055 *N*.

TABLE III

Tin taken g.	Titanium added, $N/50$ $TiCl_3$ ml.	Standard iodine solution ml.	Tin found g.	Error high Per Cent.
0·0119	Nil	18·95	0·0119	—
,,	0·5	19·10	0·0120	0·8
,,	1·0	19·38	0·0122	2·5
,,	2·0	19·40	0·0122	2·5
,,	5·0	19·87	0·0124	5·0
,,	10·0	19·97	0·0125	5·0

It will be noticed that the increase of titanous chloride from 5 ml. of *N*/50 solution to double that amount produced no additional increase in the amount of iodine used.

Table IV shows the effect of the addition of 5 ml. of *N*/50 titanous chloride solution to 10 ml. of *N*/50 stannous chloride solution. Both were titrated with

$N/100$ iodine solution, but two different solutions, similarly prepared, were employed.

TABLE IV

$N/100$ Ordinary iodine solution, standardised against tin

Iodine solution	Tin taken g.	Titanium added, $N/50$ $TiCl_3$ ml.	Titration, $N/100$ iodine ml.	Tin found g.
A	0·0119	Nil	18·95	0·0119
	,,	5·0	19·87	0·0125
B	,,	Nil	18·60	0·0119
	,,	5·0	20·24	0·0129

This shows that different values were obtained for the titanium effect when two iodine solutions, similarly prepared, were used. In view of this difference, it is not surprising that different assayers have disagreed about the magnitude of the titanium effect.

In Tables III and IV the iodine solution was standardised against tin. In Table V are shown the results obtained when the iodine solutions were standardised against arsenious oxide.

TABLE V

$N/100$ Ordinary iodine solution, standardised against As_2O_3

Iodine solution	Tin taken g.	Titanium added, $N/50$ $TiCl_3$ ml.	Titration, $N/100$ iodine ml.	Tin found g.
A	0·0119	Nil	18·95	0·0112
	,,	5·0	19·87	0·0118
B	,,	Nil	18·60	0·0108
	,,	5·0	20·24	0·0118

These results show that, if the true iodine strength of the solution is taken as standard, instead of the empirical standardisation against tin, low results are obtained when tin is titrated. The addition of titanium raises the titration to the stoichiometric figure. Paradoxical as it may sound to assayers, who have been accustomed to regard titanium as an undesirable impurity in tin assays, it is possible to obtain correct results by using the true iodine value of the solution and adding titanous chloride to the assay solution. Titanous chloride, like antimony chloride, is apparently a negative catalyst for the reaction between stannous chloride and oxygen.

It will be noticed that the amount of the titanium effect is different with the two iodine solutions; but that when arsenious oxide is used to standardise the iodine solution, the discrepancy is due to a variable error in the titration when titanium is absent. In presence of titanium, consistent results are shown by both solutions. The difference is evidently due to a difference in the amount of oxygen dissolved in the two iodine solutions.

When an air-free iodine solution is used, the addition of titanium produces no effect on a tin assay.

Results obtained with air-free $N/100$ iodine are shown in Table VI.

TABLE VI

Tin taken g.	Titanium added, $N/50$ $TiCl_3$ ml.	Tin found g.
0·0119	Nil	0·0118
		0·0118
	5·0	0·0119
		0·0119
		0·0120
0·0237	Nil	0·0238
		0·0239
	5·0	0·0238
		0·0239
		0·0239

It has been shown by Tomiček[12] that cuprous chloride catalyses the reaction between titanous chloride and iodine. It might, therefore, be expected that the presence of copper in a tin assay would cause a high result when titanium is also present. The figures in Table VII shows that, with small amounts of copper, this effect is not apparent.

TABLE VII

Tin taken g.	Titanium added, $N/50$ $TiCl_3$ ml.	Copper added g.	Tin found g.
0·0237	5·0	Nil	0·0239
		0·0001	0·0238
		0·0004	0·0239
		0·0008	0·0239
		0·0008	0·0240
		0·0010	0·0239

If all the titanous chloride reacted with iodine it would correspond to an increase of the tin found by 0·0059 g. We have not further studied the effect of copper.

PREPARATION OF AIR-FREE IODINE SOLUTION.—About 1100 ml. of distilled water were boiled in a flask, A, Fig. 1, in presence of a gentle current of carbon dioxide from a suitable generator, for about an hour. The clip (*a*) was then closed, and the flask cooled to a few degrees below laboratory temperature while still connected with the supply of gas. The flask was shaken occasionally until the water was saturated with gas, as shown by no alteration in the acid level of the generator on further shaking.

The necessary quantity of potassium iodide was placed in the graduated litre flask, Fig. 2, B, provided with an extra mark to allow for the volume of the weighing bottle carrying the iodine. The flask was then cleared of air by displacement with carbon dioxide, through a tube (*b*) reaching nearly to the bottom. The weighing bottle, carrying the iodine, was then dropped in, and the gas leading tube (*b*) was changed for a shorter, drawn-out tube (*c*), connected with the long tube (*d*) of the air-free water flask, A, by means of a length of black rubber tube carrying a pinch-cock (*e*). The rubber tube had been previously filled with water by raising the pressure on the gas generator, by means of a rubber-bulb connected with the acid side of the generator. The transference was made against a current of carbon dioxide led in through (*f*). For the sake of avoiding repetition we may here explain that all operations involving the breaking of a joint or transference of liquid were made against a counter-current of carbon dioxide or the back pressure from a second generator.

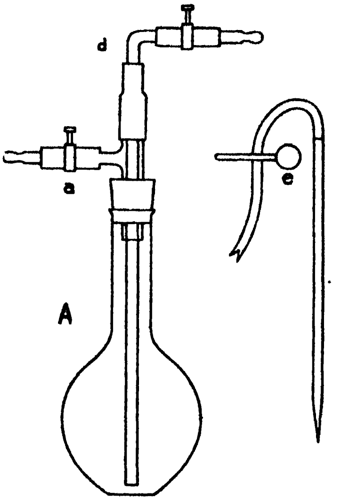

Fig. 1.

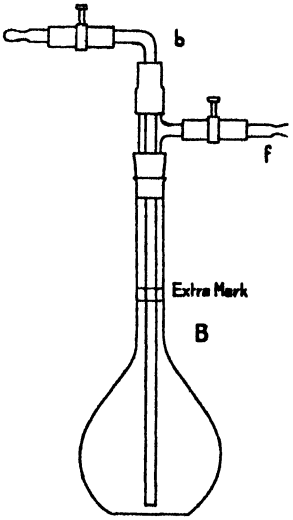

Fig. 2.

A little water was first run in to supply concentrated potassium iodide for solution of the iodine; this effected, the bulk was made up to the mark, shaken and transferred to the stock-bottle of a self-filling burette, arranged for the preservation of the solution under carbon dioxide, the stock-bottle and burette being first cleared of air by the same method.

No trouble was experienced from contact of iodine with rubber connections, provided that red rubber pressure-tube was used. Black, lightly vulcanised tube was unsatisfactory. Red rubber is not entirely free from attack by iodine, but was found soon to reach a condition in which no further action could be detected.

The carbon dioxide was prepared from marble and hydrochloric acid.

METHOD FOR REDUCTION OF TIN SOLUTIONS PREVIOUS TO TITRATION.—To the solution of tin chloride, contained in a 300-ml. round, flat-bottomed flask were added 20 ml. of concentrated hydrochloric acid (1·16 sp.gr.), 25 ml. of water, and 1 g. of aluminium turnings. After about an hour, when the action of the acid on the aluminium had almost ceased, 20 ml. of concentrated hydrochloric acid were added, a cork carrying an eduction tube was fitted, and the contents of the flask were heated to boiling. When the remaining aluminium and the precipitated tin had dissolved, the eduction tube was connected with a supply of carbon dioxide while steam was still issuing (Beringer, *Text-book of Assaying*, 1908), and the flask was cooled in a bath of cold water. When cold, the solution was immediately titrated without further special precautions.

Tin solutions cooled and titrated under the above conditions gave stoichiometric results with air-free iodine solutions, standardised against arsenious oxide; proving that the stannous chloride was completely reduced and suffered no oxidation by air during cooling or titration (*cf.* Table VI).

SUMMARY.—We have shown that low results in tin titrations are due, not to incomplete exclusion of gaseous oxygen from the titration flask, but to oxygen dissolved in the iodine solution.

The various methods that have been advocated for the improvement of tin titrations are, in effect, methods of preventing the reaction of dissolved oxygen. This has not always been the avowed object of the investigators. For instance, Ibbotson and Brearley[13] used antimony as a reducing agent; the antimony chloride formed was subsequently shown by Kolthoff[6] to be a negative catalyst for the oxygen reaction. From their paper, however, it is clear that they had quite different ideas as to why the antimony reduction gave good tin titrations.

It will probably be generally agreed that:

1. A stoichiometric titration for the determination of an element is preferable to one in which there occurs a constant error, neutralised by standardising the volumetric solution under the same conditions as for assays.
2. A direct titration is preferable to a determination made by addition of excess of a reagent, followed by back-titration.
3. The standard solution should contain no impurity that interferes with a titration; in this instance, oxygen.

The above considerations lead to the conclusion that the best method of titrating stannous chloride is by means of an air-free solution of iodine.

The general argument, so far as tin is concerned, is re-inforced by the following specific consideration:

The assumption that the oxygen interference is a constant effect, which can be neutralised by standardisation of the iodine solution against tin, is not justified in the assaying of tin ores. Titanium is the main cause of inconstancy of the oxygen effect; and this is the only interference that titanium, by itself, exerts on tin assays. The removal of titanium from a tin ore involves a troublesome separation, which is unnecessary when an air-free iodine solution is used for titration.

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DISCUSSION

Dr. J. J. Fox said that many years ago Dr. Farmer had described how to obtain air-free water by bubbling carbon dioxide through it.

Dr. B. S. EVANS said that he regarded the paper as a valuable contribution to the literature of the subject. There were, however, certain points that were not clear to him. He understood that starch was the indicator used; his own experience of starch was, first that it required an appreciable amount of iodine to produce the colour; and, secondly, that its sensitiveness varied enormously with the proportion of potassium iodide present; if the potassium iodide-content were reduced, the end-point might be affected. The question of air in the iodine solution had not occurred to him, and he would not have thought that it could exert such an influence. As regards the effect of other elements, he thought that it was generally desirable to make a preliminary separation of the tin; the presence of copper, at any rate, was fatal to accuracy. He assumed that the antimony mentioned was the chloride and not the metal, for it had been shown conclusively that metallic antimony would interfere with the titration. With regard to the reduction with aluminium, he, personally, regarded all reductions of tin with metals as suspect. He understood that his own figures obtained with hypophosphite reduction were not challenged.

THE AUTHORS (in a written reply) say: The indicator was prepared from potato starch, which had been rendered soluble by treatment with 2 per cent. v.v. hydrochloric acid. The sensitiveness of the starch-iodide end-point was influenced by the concentration of potassium iodide. All their iodine solutions were $M/5$ with respect to potassium iodide. This provided sufficient for a sharp end-point in the assay solution, with the smallest quantity of standard solution used in a titration. "Blanks," with the same quantity of potassium iodide added, gave an end-point with one drop of $N/100$ iodine solution.

The antimony mentioned in connection with its catalytic action was in the form of chloride. The figures obtained by Dr. Evans by means of hypophosphite reduction were not questioned in any way. The object of the paper was to show that the direct titration of stannous chloride by iodine could be affected by an error which had been generally overlooked, namely, the presence of air in the standard solution. Dr. Evans's work was carried out under conditions very different from theirs, and they had made no study of them; but, in view of their results, it seemed probable that his stoichiometric figures were due to the high dilution employed, the low concentration of acid and potassium iodide; or, possibly, to the fact that hypophosphorous acid acted as an anti-catalyst in the oxygen and stannous chloride reaction.

With regard to metallic reducers, their figures showed that reduction with aluminium was complete. In this connection the possibility of attributing a low result, caused by air in the standard solution, to incomplete reduction by a metal, should not be overlooked.

31 CANNON'S DRIVE
EDGWARE, MIDDLESEX

The Determination of Magnesium in Duralumin

By G. STANLEY SMITH, B.Sc., A.I.C.

In the analysis of aluminium alloys the determination of magnesium often causes much trouble. It is usually estimated in the residue left after a caustic soda attack, elements interfering in the phosphate precipitation being removed by the group reagents or held in solution by the addition of tartaric acid. Re-precipitations, with the consequent accumulation of ammonium salts in the solution are necessary if aluminium, iron and manganese are removed by means of bromine and ammonia or of ammonia and ammonium sulphide, and it is by no means easy to get rid of all the manganese. The magnesium ammonium phosphate must in any case be precipitated twice and the ignited pyrophosphate examined for manganese.

The method to be described eliminates reprecipitations and is rapid and simple, and the results are trustworthy. The removal of aluminium, iron and manganese from a dilute sulphuric acid extraction of the caustic soda residue is accomplished by means of zinc oxide and potassium permanganate, as in a Volhard titration, but without the need for obtaining an exact end-point, the excess of permanganate being removed by alcohol. Magnesium hydroxide is then thrown down in the filtrate by means of sodium hydroxide and potassium cyanide, the latter serving to keep in solution any copper or nickel. The precipitate is dissolved in dilute acid, and the magnesium is determined as pyrophosphate or, less accurately, by adding excess of $N/10$ sodium hydroxide solution to the neutral solution and titrating the excess in a portion of the clear solution.

Since the magnesium ammonium phosphate is precipitated in an almost pure solution of magnesium sulphate, a reprecipitation is unnecessary. The time required for a determination, including a standing period of 4 hours for the precipitation, is about 7 or 8 hours. If the volumetric method is used, the time can be reduced to about 2 hours.

Method.—Dissolve 2 g. of the alloy in 60 to 70 ml. of sodium hydroxide solution (10 per cent.). Filter through a 9-cm. Whatman, No. 40, filter-paper, and wash thoroughly with hot water. Hold the funnel in a horizontal position and, without removing the paper, wash back the insoluble residue into the original beaker with hot water. Add 5 ml. of dilute sulphuric acid (sp.gr. 1·2), boil for about a minute, pour the solution through the paper, and wash the residue of copper with hot water. The residue contains no magnesium, but a little copper is certain to go into solution. To the filtrate add sodium hydroxide solution until a slight precipitate forms. Clear the solution with a drop of dilute sulphuric acid and run in from a burette $N/10$ or $N/20$ permanganate to oxidise the iron. Boil the solution and add zinc oxide emulsion in slight excess. Continue the addition of permanganate to the nearly boiling solution until the liquid is coloured pink and remains pink on further boiling and on the addition of a little more zinc oxide. Then add 2 or 3 drops of alcohol and boil again for a few minutes to remove the permanganate. Filter the solution and wash with hot water. The filtrate is free from aluminium, iron and manganese, but contains a little copper not precipitated by zinc oxide, and also nickel, if present in the alloy. Add about 1 g. of potassium cyanide and 10 ml. of 10 per cent. sodium hydroxide solution, boil for 2 or 3 minutes, introduce about half a 9-cm. filter-paper as pulp, mix well, filter after standing a short time, using a 9-cm. paper, and wash several times with 1 per cent. sodium hydroxide solution. The solubility of magnesium hydroxide is negligible in the presence of alkali. Transfer pulp and precipitate to the beaker without removing the filter-paper, add rather more dilute sulphuric acid than is needed to give an acid reaction to methyl orange, stir well to make sure that the magnesium hydroxide has dissolved, pour through the same filter-paper, and wash with hot water. Add a little ammonium chloride and then ammonia to make the solution slightly alkaline. The absence of a precipitate confirms the completeness of the separation of aluminium and iron by zinc oxide. Make slightly acid, add a small quantity of microcosmic salt or ammonium phosphate, boil and add an excess of ammonia. Leave the solution for about 4 hours, filter through a No. 40 paper, wash with 2 per cent. ammonia, ignite and weigh the magnesium pyrophosphate.

Instead of the magnesium being precipitated as phosphate it may be determined speedily by titration, the results being sufficiently accurate for most purposes. After dissolving the hydroxide in sulphuric acid add dilute sodium hydroxide solution till the reaction is alkaline, make acid with *N*/10 sulphuric acid, boil to remove any carbon dioxide, cool and make the solution exactly neutral by means of *N*/10 acid and alkali, using a reference solution to obtain the correct tint of methyl orange. Transfer to a 250-ml. volumetric flask, run in 50 ml. of *N*/10 sodium hydroxide solution, fill to the mark, and mix. After about 10 minutes filter off 200 ml. and titrate the excess of alkali with acid (1 ml. *N*/10 NaOH ≡ 0·001216 g. Mg.).

The method has been tested on a large number of dural samples, in which the magnesium-contents varied from 0·35 to 0·80 per cent. The results obtained by the gravimetric method agreed to the second decimal place with those obtained by other satisfactory methods. By the volumetric method slightly higher results were usually given, to the extent of 2 or, at most, 3 units in the second place. These are explained by the impossibility of separating zinc completely from magnesium by a single treatment with sodium hydroxide and cyanide; also, by the difficulty of obtaining the exact end-point in the titration. Methods of titrating solutions of magnesium salts are discussed by Kolthoff.[1]

Results obtained by the gravimetric method with a solution of the sulphates of the various metals are shown in the table below. In precipitating magnesium

Elements present (weight in g.):

	Al	Fe	Mn	Cu	Ni	Mg	Mg. found
(i)	—	—	—	—	—	0·0255	0·0255
(ii)	0·01	0·02	0·025	0·01	—	0·0255	0·0256
(iii)	0·10	0·02	0·025	0·01	0·01	0·0255	0·0255
(iv)	0·05	0·04	0·05	0·02	0·02	0·0255	0·0256
(v)	0·01	0·02	0·025	0·01	—	0·0510	0·0511
(vi)	0·25	0·04	0·05	0·02	0·02	0·0010	0·0014

hydroxide with sodium hydroxide the reagent was added in quantity sufficient to redissolve the zinc hydroxide.

In (vi) the pyrophosphate contained a little zinc, but none of the magnesium had been lost.

The magnesium pyrophosphate precipitate has been repeatedly tested for manganese, but in no instance has more than the equivalent of 1 drop of $N/20$ potassium permanganate solution been found—an amount which may be regarded as negligible. According to Sarkar and Dhar[2] a compound $2MgO, 7MnO_2, xH_2O$ (where $x = 19$ or 13) is formed by the interaction of permanganate with a solution of a manganese salt containing magnesium. The formation of such a compound would obviously invalidate the method described. In no instance, however, has the manganese precipitate, produced in the presence of a slight excess of zinc oxide, contained more than a trace of magnesium.

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Notes

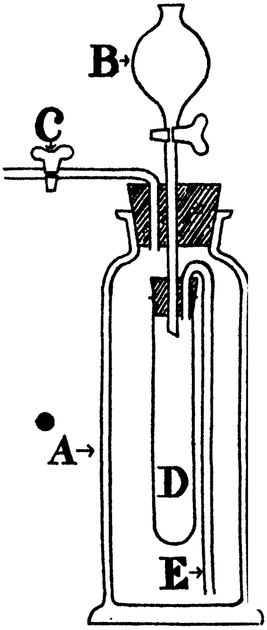
The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

METHOD FOR DETERMINING "AVAILABLE" AND "TOTAL" CARBON DIOXIDE IN BAKING POWDERS AND SELF-RAISING FLOURS

THE published methods for these determinations are, in the main, lengthy, or require special apparatus, or are not very accurate. The method now to be described is essentially a modification of that given by Hepburn (ANALYST, 1926, **51**, 622), and the interpretation of "available" carbon dioxide is that suggested by Liverseege (*Adulteration and Analysis of Food and Drugs*, p. 435).

APPARATUS.—The apparatus consists of a tall thick-walled glass vessel, A (an absorption tower of 400 ml. capacity is suitable), fitted with a tap funnel, B, and a glass tap, C. The funnel stem runs directly into a stout glass boiling tube, D (about 50 ml. capacity), from which a delivery tube, E, leads almost to the bottom of A.

METHOD.—A suitable quantity of the sample (0·2 to 0·3 g. of baking powder or about 3 g. of self-raising flour) is weighed into the tube, D, 50 ml. of $N/10$ barium hydroxide solution and about 50 ml. of carbon dioxide-free water (to increase the column of absorbing liquid) are placed in A, and the apparatus is assembled as shown in the diagram, and then evacuated for about 10 minutes. (It is essential that the apparatus should be air-tight, otherwise the liquid in A may be forced back into D.) The glass tap, C, is then closed, and 20 ml. of water (for "available" carbon dioxide) or 20 ml. normal hydrochloric acid (for "total" carbon dioxide) are run in very gradually from the tap funnel while the apparatus is gently shaken. The liberated carbon dioxide is mainly absorbed by the baryta as the gas bubbles through it. The absorption is allowed to proceed with occasional shaking, to prevent surface saturation and to quicken absorption, for 3½ to 4 hours, a period which we have found to be adequate. At the end of this time the vacuum is destroyed by gradually opening the tap of the funnel, the rubber bung and attached tubes are removed, their surfaces being rinsed into A with a little water, and the residual baryta is titrated with $N/10$ oxalic acid, phenol-thymolphthalein being used as indicator.* A point to note, and one not very generally known, is that this indicator (pH 8·3 to 11·0) is most satisfactory for acid-alkali titrations where interference of carbonates is to be avoided; the end-point is distinct and the colour-change sharp, from deep blue to colourless. In our experience phenolphthalein gave a very indefinite end-point owing to repeated fading.



"Total" carbon dioxide can be determined on the same quantity of the sample by pipetting a fresh quantity (50 ml.) of $N/10$ baryta into the bottle, A, and replacing the tube in position. After evacuation of the apparatus as before, 20 ml. of normal acid are run in very cautiously and the liberated carbon dioxide is determined as before. The difference between the "available" and "total" carbon dioxide in most cases is, however, small, and therefore we make a practice of determining the latter on a fresh quantity of the sample.

In Table I are recorded results obtained with freshly-ignited sodium carbonate, A.R. It will be seen that between 96 and 99 per cent. of the carbon dioxide is absorbed in 2 hours, and that total absorption takes place in 3½ to 4 hours. No appreciable difference was observed in the time for complete absorption by doubling the quantity of baryta (Experiment 6).

Baking Powders.—In connection with these analyses (Table II) we examined some tartrate and some phosphatic powders to make certain that 4 hours were adequate for the latter, as they liberate their carbon dioxide rather slowly.

Self-raising Flours.—Since the sale of this article was legalised by the Bread Acts Amendment Act, 1922, its use has steadily increased, but no attempt has yet been made to fix any standard for the "available" carbon dioxide on which the value of such an article depends. No such attempt was made in the Agricultural Produce (Grading and Marking) (Wheat Flour) Regulations, 1933, which requires that self-raising flour "shall contain such ingredients or mixture of ingredients in such quantities and proportions as are properly required to make the flour self-raising."

In the determination of "available" carbon dioxide in self-raising flour, water should be added very cautiously to avoid frothing over. The use of alcohol (*cf.* Callan, ANALYST, 1927, **52**, 222) to prevent frothing was not found satisfactory.

SUMMARY.—1. A simple method is described for the determination of "available" and "total" carbon dioxide, requiring no special apparatus and little manipulation, applicable to a small quantity of sample and sufficiently accurate to give results agreeing to within 0·1 per cent. of the theoretical.

2. The apparatus devised, being entirely rigid and without loose parts, is easy to handle, and as the CO_2 liberated is actually made to bubble through the

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* We also tried thymolphthalein whose pH range (9·3 to 10·5) is somewhat similar, but the colour-change is not nearly so sharp, owing to the blue colour in alkaline solution being very faint.

baryta solution, the period for complete absorption is shortened to only 4 hours as against 12 to 24 hours in Hepburn's method.

3. The indicator phenol-thymolphthalein offers distinct advantages over phenolphthalein and thymolphthalein.

TABLE I

EXPERIMENTS WITH FRESHLY-IGNITED SODIUM CARBONATE

(Theoretical CO_2-content 41·52 per cent.)

Time of absorption Hours	Weight taken g.	$N/10$ baryta used ml.	Carbon dioxide found Per Cent.
16	0·111	20·95	41·52
24	0·106	20·00	41·51
1½	0·090	16·35	39·96
2	0·098	18·35	41·19
2	0·198	36·40	40·45
2	0·101	18·60*	40·51
3	0·109	19·80	39·96
3½	0·097	18·65	41·45
4	0·099	18·65	41·45
4	0·098	18·45	41·42
4	0·100	18·85	41·48
4	0·106	20·00	41·51
4	0·197	37·10	41·43

* Double quantity (100 ml.) of baryta taken.

TABLE II

BAKING POWDER

Sample	Type of raising ingredient	"Available" CO_2 found		"Total" CO_2 found
		4 hours Per Cent.	16 hours Per Cent.	4 hours Per Cent.
Baking powder 1	Tartrate	9·20	9·20	9·40
,, ,, 2	,,	8·97	8·90	11·10
,, ,, 3	,,	10·31	10·39	10·90
,, ,, 4	,,	8·33	8·17	9·60
,, ,, 5	Phosphatic	3·67	3·70	4·30
,, ,, 6	,,	6·50	6·41	7·90
,, ,, 7	,,	4·49	4·60	5·60

TABLE III

SELF-RAISING FLOUR

Sample	Available carbon dioxide found	
	4 hours Per Cent.	16 hours Per Cent.
Self-raising flour 1	0·35	0·38
,, ,, 2	0·31	0·32
,, ,, 3	0·35	0·40

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EXTRACTION OF LEAD BY MEANS OF DIPHENYLTHIOCARBAZONE

In the examination of foodstuffs and biological materials for traces of lead by wet oxidation with sulphuric and nitric acids, followed by the diphenylthiocarbazone extraction method of Allport and Skrimshire (ANALYST, 1932, 57, 440), considerable difficulty has frequently been experienced in the colorimetric matching of the final solutions.

This trouble was encountered in the examination of organs by Roche Lynch, Slater and Osler (ANALYST, 1934, 59, 787), and they had not been able to devise a method for its removal. The colour developed is probably due, as they suggest, to nitro bodies which are resistant to further oxidation by nitric and sulphuric acids, and are extracted by the chloroform. Possibly the interfering colour may be avoided by using other methods for oxidation of the original material, but for large bulks these prove tedious.

The following method has been developed and used with complete success for some time. The residues obtained after evaporation of the chloroform are warmed with 2 ml. of concentrated sulphuric acid on a water-bath for a few minutes to destroy the organic compound, 10 ml. of 6 per cent. hydrogen peroxide are added, and the mixture is boiled until white fumes are evolved. After addition of 2 g. of pure ammonium persulphate the flask is heated on an asbestos gauze over a Bunsen burner for half an hour. The resulting solution is colourless, and does not develop any yellow tint with ammonia. D. C. GARRATT

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Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

GIBRALTAR

REPORT OF THE CITY ANALYST AND BACTERIOLOGIST FOR THE YEAR 1934

THE total number of specimens and samples examined during the year was 4589, of which 102 were samples of food and drugs.

GOATS' MILK.—Of the 48 samples of milk taken by the sanitary inspectors, 40 were of goats' milk and 8 of cows' milk. The statutory limits for goats' milk are: Fat, 3·5; non-fatty solids, 8·0 per cent. The average composition of the samples examined was: Milk fat, 4·34; non-fatty solids, 8·83 per cent.

IMPORTED UNBOILED MILK.—No sample of imported milk was found to be wholly unboiled. Of the 28 samples examined, 4 contained 8, 4, 3, and 3 per cent. of unboiled milk, respectively. The Public Health Ordinance demands that all imported milk shall be "boiled, pasteurised or sterilised."

The Ortol Test for Unboiled Milk.—Further experimental work on the ortol test for the detection and estimation of small quantities of unboiled (raw) milk in boiled milk has been done. Varying degrees of brick-red colour are obtained according to the amount of unboiled milk present. The colour obtained with boiled milk containing from 1 to 20 per cent. of unboiled milk can readily be matched if the control admixtures (*i.e.* boiled milk plus raw milk) are made previously and are ready to receive the ortol and hydrogen peroxide at the same time as the sample under examination. The question arose whether by heating a raw unboiled milk at various possible temperatures and varying the duration of heating, the enzymes (responsible for the deep brick-red colour given by raw milk) could be partly destroyed. This would mean that only a partial red colour would be obtained and mislead the analyst to assume that a percentage of raw milk was present. Under the conditions applicable to Gibraltar, it may be necessary to give evidence on this point in court. I tried to match the depth of colour given by a boiled milk containing 8 per cent. of unboiled raw milk, and found that this was possible by heating raw milk to 73° C. for 10 minutes.

Below are given the results obtained by heating raw milk at different temperatures for varying lengths of time and quickly cooling it before adding ortol and hydrogen peroxide.

Temperature ° C.	Duration of heating Minutes	Colour obtained with ortol and hydrogen peroxide
70	30	Full, as for raw milk
72	15	Full, as for raw milk
72	30	Half, as for 50 per cent. raw milk (approx.)
73	10	Partial, as for 8 per cent. raw milk
73	20	Slight, as for 1 per cent. raw milk
73	30	None, as for boiled milk
75, 76, 77	25	None, as for boiled milk
75, 76, 77	20	Some, as for 2 per cent. raw milk
80, 82, 83	10	None, as for boiled milk
80, 82, 83	5	Slight, as for 1 per cent. raw milk
84	5	None, as for boiled milk
85	1	None, as for boiled milk

The ortol test does not show whether a milk has been pasteurised (62·8°–65·5° C. for ½ hr. and quickly cooling), and the lowest temperature with 30 minutes' heating which gave no colour with ortol was 73° C.

In making these tests 10 ml. of milk were heated in a test-tube in a water-bath. The milk was quickly cooled before adding the ortol (0·5 ml. of 5 per cent. solution) and hydrogen peroxide (1 to 5 drops of 10 vol. solution). Three minutes were allowed for colour to develop. Too much hydrogen peroxide tends to destroy the colour.

ICE CREAM.—Inspection of the ice creams sold in Gibraltar was undertaken, and four different supplies were bacteriologically examined. It is not at present practicable to lay down definite bacteriological standards, but, as a rough guide, Buchan has suggested that ice creams made under clean conditions shall

(1) not contain more than 1,000,000 organisms per ml. growing at 73° C.
(2) not contain *B. coli* in less quantity than 0·1 ml.;
(3) not contain streptococci in less quantity than 0·001 ml.;
(4) not contain *B. enteritidis sporogenes* in less than 10 ml.

The results obtained from the four samples of ice cream examined were as follows:

	No. 1	No. 2	No. 3	No. 4
Total organisms growing at 37° C. per ml.	41,610	110,400	2,110,000	4,992,000
B. coli	In 0·1 ml.	In 0·1 ml.	In 0·000001 ml.	In 0·00001 ml.
Streptococci	In 0·01 ml.	In 0·1 ml.	In 0·1 ml.	In 0·1 ml.
B. enteritidis sporogenes	Not in 30 ml.	Not in 30 ml.	Not in 30 ml.	Not in 30 ml.

Ice creams Nos. 1 and 2 were considered satisfactory, but Nos. 3 and 4 were not up to the desired bacteriological standards.

ANTHRAX IN SHAVING BRUSHES.—Samples of tooth brushes purchased from shops contained no anthrax bacilli, and were found to be sterile. Shaving brushes were also examined. One sample was found to be infected with *B. anthracis*, and the consignment was withdrawn from sale.

A. G. HOLBOROW

CITY OF SALFORD

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1934

THICK CREAM.—A sample of tinned cream, labelled "Pure Thick Cream," contained 20 per cent. of fat. Although the average purchaser would associate (perhaps subconsciously) the word "thick" with a high fat-content, it is obvious that proceedings would be likely to fail, since the producers could say that "thick" referred to the physical condition. It is suggested that the following standards should be set up for cream (including tinned cream):

Double (or thick) cream ..	50 per cent. of butter-fat
Thin cream	20 ,, ,, ,,

BOOK LICE IN FLOUR.—A sample of self-raising flour was found to contain live insects which were identified at the Zoology Department, Manchester University, as the common book louse. This insect derives its name from the fact that it frequents the bindings of books, where it lives upon the starchy paste; it is not harmful. The insects probably got into the flour in the shop, and the shopkeeper was therefore advised to give the shelf and its vicinity a thorough cleansing with disinfectant.

CASTOR OIL PILLS.—A formal and an informal sample contained not more than 2 per cent. or 1/10 minim of castor oil per pill. As the medicinal dose is 60 to 480 minims, it is obviously impossible for a pill to contain even a moderate dose of the oil. Powders and pills containing the active principle of castor oil have had only a limited sale. The particular pills approximated in composition to the compound rhubarb pill of the B.P., and after an interview the manufacturers agreed to label them as "Aperient Pills"—and to add, in smaller type, "a substitute for castor oil."

LYSOL.—Four of 5 samples of lysol submitted were adulterated. They contained 2·2 to 2·8 per cent. of cresol. Two stated on the label that they contained not more than 3 per cent. of cresols, and one claimed to be "approved by Health Authorities."

In the original patent for lysol by Dammann in 1891 no strength was specified, but the only strength prepared by the patentee was 50 per cent. of cresols in a soapy solution, and when, after 1914, a number of British firms prepared lysol, this was the strength adopted by them all. If the standard in the B.P. 1932 is compared with the amounts of cresols in the samples mentioned above, it will be seen that they contain about 1 part of lysol in 20 parts of water. In the dilution recommended, namely, one tablespoonful to the pint, they would be practically useless as disinfectants.

Summonses under the Merchandise Marks Act, 1887, were issued against the retailers of three samples for selling an article to which a false trade description was applied, and against the makers for applying a false trade description. The makers and wholesalers were also summoned under the Summary Jurisdiction Act, 1848, for aiding and abetting, counselling and procuring the retailer in the sale, and convictions were obtained (*cf.* ANALYST, 1934, **59**, 693).

LYSOL SOAP.—Four samples, purchased as lysol soap, contained the following amounts of cresols:

Cresols, per cent. ..	2·8	0·25	0·6	0·8
equivalent to lysol, per cent.	5·6	0·5	1·2	1·6

Experiments were made to determine the minimum percentage of lysol in a soap which would justify its being called "Lysol" soap. The usual dilution of "Lysol" recommended for washing the hands is 1 per cent., and a 0·5 per cent. solution is stated to have a disinfectant action upon the skin. Therefore a lysol soap might reasonably be expected to be one which, in use, results in at least a 0·5 per cent. solution of lysol being applied to the skin. An estimation of the amount of lather left on the hands after rubbing with soap at 50° C., so as to form a good lather, gave the following results:

Time of lathering Seconds	Total solids in lather Per Cent.	Equivalent of soap (on basis of 30 per cent. water)
5	10·6	15
10	16·1	23

In the average use of soap the percentage of soap in the lather formed is thus not likely to exceed 25. For this lather to contain 0·5 per cent. of lysol, the soap must contain not less than 2 per cent. of lysol. On this basis it is reasonable to conclude that a reasonably good lysol soap contains not less than 4 per cent. of lysol, and that 2 per cent. is a minimum standard.

PHENOLATED IODINE SOLUTION.—A sample contained: iodine, 0·05; potassium iodide, 0·5; and phenols (as cresylic acid), 0·5 per cent. Although there is no standard for this article, it was so deficient in all its constituents that it was condemned as adulterated. A reasonable standard would be: iodine, 2·5; phenol, 2 per cent. A sample previously examined passed this standard.

H. E. MONK

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE SECOND QUARTER, 1935

OF the 1362 samples of foods and drugs examined, 1293 were bought informally and 69 formally.

SULPHUR DIOXIDE IN BLACKCURRANT JAM.—A sample contained 50 p.p.m. of sulphur dioxide. The firm explained that blackcurrant pulp was very tenacious of the sulphur dioxide used as a preservative, and that representations to this effect had been made to the Ministry of Health by a number of firms with a view to getting the permissible amount allowed in blackcurrant jam raised to 100 parts per million, but without success. The firm was now incorporating with the pulp a proportion of blackcurrants preserved by heat, to prevent an undue amount of sulphur dioxide appearing in the finished jam.

TIN IN SILD IN OLIVE OIL.—An informal sample contained 5·3 grains of tin per lb., and a formal sample 5·4 grains. Both tins were badly corroded. A report to the Local Government Board in 1908 by Drs. Buchanan and Schryver (*cf.* ANALYST, 1909, **34**, 121) stated that the presence in food of more than 2 grains per lb. of tin might be taken to signify that it had become potentially deleterious to health and these samples were, therefore, condemned.

Correspondence with the wholesale dealers concerned elicited the information that this was the first complaint received by them, although millions of tins had been imported by them from Norway. The tinplate used was of English manufacture. They were writing to the Norwegian suppliers in order to try and trace any possible source of the trouble.

"NON-TANNIC" TEA.—The label on the packet of a sample of tea contained the statements that it was "Non-tannic," "Free from stalk which contained crude tannin," and "Digestive because non-tannic." The amount of tannin was 16 per cent., a figure rather higher than the average. Correspondence with the firm responsible for the packing is still proceeding, but the words "Non-tannic" have already been withdrawn in the latest type of package. H. H. BAGNALL

Ministry of Health

Sale of Food and Drugs

EXTRACTS FROM THE ANNUAL REPORT FOR 1934–1935, AND ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1934*

THE total number of samples analysed by Public Analysts in England and Wales during 1934 was 140,583, and of these, 7451 (5·3 per cent.) were reported against, *i.e.* a slight decrease over those of the previous year (5·5 per cent.).

PRESERVATIVES.—Of 418 contraventions of the Public Health Regulations, the added preservative would have been permissible in 152 cases (148 of sausages) if it had been properly declared. Boron in cream, milk, ice-cream, biscuits, sausages, tripe, potted meat, wines, etc.; sulphur dioxide in cream, barley, pepper, minced, potted and other meats, and formaldehyde in milk were reported. A "tripe bleach" consisted of sodium perborate; and 2 samples of a "preservative liquid" were 4·5 and 4·7 per cent. aqueous solutions, respectively, of formaldehyde.

MILK.—Of 76,930 samples, 5506 were reported adulterated or not up to standard. Of the 1020 "appeal-to-cow" samples, 342 were below the presumptive standard of the Sale of Milk Regulations. Visible dirt was present in 8 samples, paraffin in 1, added colouring matter in 12, formaldehyde in 18, and boron preservative in 3. Twenty-two samples of graded milks were deficient in fat, and 25 skimmed milks and 1 buttermilk were reported against.

CONDENSED AND DRIED MILK.—Only 22 of 1098 samples of condensed milk were reported against, including unsound samples (one a milk containing tin in a blown tin), and 7 samples of dried milks.

CREAM.—Of 2024 samples examined, 11 contained boron preservative, 5 sulphur dioxide, 1 added colouring matter, 1 tin, and 1 sample 1·53 per cent. of lactic acid. Two samples were deficient in butter-fat, and 2 samples labelled "Pure Thick Cream" and 1 "Thick Rich Cream" were considered to be too poor in fat to justify the labels.

BUTTER AND MARGARINE.—Of butter, 73 of 8612 samples, and of margarine, 23 of 3013 samples, were reported against, mostly for containing excess of water.

LARD AND OTHER FATS.—Adverse reports on 10 samples out of 2675 were accounted for by 7 samples consisting wholly or partly of foreign fat, 1 containing 1·2 per cent. of water, and 2 containing excess of free fatty acids. Excess of rice flour or other starchy material was present in most of the 39 incorrect suet samples (of 490 examined), whilst of the 524 samples of dripping, 1 consisted wholly of vegetable fat, 1 had an excess of free fatty acids, and 8 contained excess of water.

CHEESE.—Of 1432 samples, 19 were reported against; 7, sold as cream cheeses, were whole-milk cheeses, and 2 samples of "double cream" cheeses had water as their principal ingredient.

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* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3d. net.

BREAD AND FLOUR.—The 275 samples of bread were all satisfactory, and of 1269 samples of self-raising flour, 1 contained 1·5 p.p.m. of lead, 1 excess of mineral matter, and 1 contained book lice.

JAM AND MARMALADE.—Excess preservative accounted for the adverse reports on 32 samples of 1486 examined, and the remaining 62 samples were mostly deficient in fruit or soluble solids.

VINEGAR.—Of 1716 samples, 173 were adulterated or below standard, which is a considerable increase over those of 1933 (98 of 1746). Deficiency in acetic acid accounted for 110 samples, and 7 samples contained vinegar eelworms, and 1 sample contained copper.

SPIRITS AND BEER.—Of 1841 samples, 72 of whisky, 25 of gin, 22 of rum, and 4 of brandy had had the spirit reduced below 35° U.P. Six beers contained excess of preservative, 5 contained excess of lead, and 1 had 0·3 per cent. of carbolic disinfectant, in a total of 496 samples.

MISCELLANEOUS ARTICLES OF FOOD.—Over 30,000 samples of other foods of very varied descriptions were examined. Nine samples sold as coffee contained chicory, 1 to the extent of 62 per cent., and 1 contained lead. Iron filings were present in several samples of tea. Many samples of "cream" confectionery were found not to contain genuine cream; 10 samples of mustard were adulterated with foreign starch; 60 samples of dried mint contained foreign leaves; facing was present in samples of barley, and 32 samples of rice contained talc and other mineral matter, dirt, acari or weevils. Adverse reports on 24 samples of fish were due to misrepresentation of names. A sample of cherry brandy was a cherry-flavoured beverage with no alcohol; dried peas contained arsenic and lead; aerated waters, cider, and canned peas and beans contained copper, and lead was found in curry powder, aerated waters and canned fish. Tin was present in canned fruit and vegetables and fish, and a sample of tinned sild contained both tin and zinc.

DRUGS.—Of 5886 samples, 286 were reported against. Thirty-two samples of sweet spirits of nitre were mostly deficient in ethyl nitrite; 16 samples of camphorated oil in camphor; iodine solution in alcohol, iodine or potassium iodide; boric ointment in boric acid; mercury ointment in mercury, and zinc ointment in zinc oxide. Calomel ointment was made with benzoated lard; a boric acid consisted of citric acid, and 2 samples of borax contained, respectively, 20 and 50 p.p.m. of arsenic. Nine samples of "lysol" were reported against, as they contained, instead of the 50 per cent. by volume of cresol of the B.P. standard, less than 3 per cent. The samples adversely reported on also included ammoniated tincture of quinine, ammoniated quinine tablets, Seidlitz, Gregory and grey powders, and bicarbonate of soda. D. G. H.

ALUMINIUM IN FOOD*

IN this Report information available upon the subject of aluminium in food has been collected and examined, with a view to reaching definite conclusions whether or not the metal is in any way injurious to health.

OCCURRENCE OF ALUMINIUM IN NATURE.—The proportion of aluminium in the earth's crust is estimated to be between 7 and 8 per cent. In agricultural soils it is usually less than this. Eight samples of soil from fields in various parts of England were found by the author to contain from 1·1 to 5·9 per cent., calculated on the dry soil. Aluminium is not a general constituent of plants, although in a few plants (*e.g.* certain club mosses, *Lycopodium clavatum* and *L. complanatum*) it is present in considerable amount. The conclusion is drawn that much of the aluminium found in plants by different workers is the result of adventitious contamination with soil and dust. Much of the aluminium found in food is also probably due to contamination with soil and dust. Coffee beans were found, by the method described below, to contain 72 p.p.m. of aluminium, but none at all after prolonged shaking with soap and water. The amount of aluminium consumed daily with food which has been properly cleaned is very small (*e.g.* 5 to 10 p.p.m.). Human and animal tissues normally contain extremely small amounts of aluminium (1 to 2 p.p.m. in all organs).

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* Reports on Public Health and Medical Subjects, No. 78. By G. W. Monier-Williams, O.B.E., Ph.D., F.I.C. Pp. 34. London: H.M. Stationery Office. 1935. Price 9d. net.

ANALYTICAL METHODS.—The chief methods, other than spectroscopic, that have been used for determining aluminium in biological material are shown in outline in a diagram. In general, the problem is one of determining minute amounts of aluminium in a precipitate of mixed iron and aluminium phosphates. The modification of the colorimetric method used by Lampitt and Sylvester (ANALYST, 1932, 57, 418) has given good results in the author's hands, although, in his opinion, colorimetric methods are less trustworthy than precipitation of the aluminium with 8-hydroxyquinoline.

The following method, depending on precipitation with 8-hydroxyquinoline, has been worked out:—A weighed quantity of the sample (25 to 100 g.) is dried and charred in a silica dish, and the char is treated with about 10 ml. of *N* sulphuric acid, dried and ashed at a low temperature in a muffle furnace. The sulphated ash is extracted on the water-bath with successive small quantities of dilute hydrochloric acid, any insoluble residue being filtered off and washed with hot water, the filter and its contents ignited in a platinum dish, the residue fused with 0·5 g. each of potassium and sodium carbonates, and the fused mass dissolved in hydrochloric acid and added to the main solution. This is evaporated in a silica dish, the residue is heated at 150° C. (to dehydrate any silica present), then cooled and extracted with moderately strong hydrochloric acid, and the liquid is filtered. The filtrate is boiled with a few drops of nitric acid (to oxidise iron) and evaporated to about 20 ml. If there is not sufficient iron present to impart a yellow tinge to the solution, 1 drop of 5 per cent. ferric chloride solution is added. If insufficient phosphoric acid is present to give an excess over that required to combine with the whole of the iron, ammonium phosphate (usually about 0·1 g. per 100 g. of sample) is added. The solution is transferred to a large boiling-tube, and dilute ammonia is run in from a burette until a slight permanent precipitate or turbidity is produced, leaving the liquid still acid (red or orange to thymol blue indicator). Three ml. of glacial acetic acid are added, the solution is heated just to boiling-point, and 5 ml. of 50 per cent. ammonium acetate solution are added gradually, with stirring, to complete the precipitation. The solution (which is now yellow) is transferred to a centrifuge tube, allowed to stand for 5 to 10 minutes, cooled and centrifuged. The supernatant liquid is decanted, the moist precipitate is shaken with hot water, cooled and again centrifuged, the mixed phosphates of iron and aluminium are dissolved in the minimum quantity of warm dilute hydrochloric acid, and the solution is diluted to about 15 ml. It is then treated with 1·25 ml. of glacial acetic acid and with 6·5 ml. of approximately 6 *N* sodium hydroxide solution (free from aluminium) to precipitate the iron as basic acetate, allowed to stand for 30 minutes, with occasional shaking, and centrifuged, the supernatant liquid being decanted. If the deposit of basic iron acetate exceeds 0·5 ml., it must be re-dissolved, the precipitation and centrifuging repeated, and the decanted supernatant liquids united.

The alkaline solution (containing the aluminium) is diluted to about 30 ml. and made just acid to bromthymol blue by adding dilute acetic acid. In the presence of 0·3 mg. of aluminium there will usually be a turbidity or precipitate of aluminium phosphate; this should be re-dissolved by adding powdered tartaric acid. Five ml. of 50 per cent. ammonium acetate solution are added, and the aluminium is precipitated by the gradual addition of a slight excess of 8-hydroxyquinoline acetate reagent [prepared by triturating 2·5 g. of the base with 5 ml. of glacial acetic acid, pouring the mixture into 100 ml. of water at 60° C., cooling and filtering (Lundell and Knowles, *Bur. Stand. J. Res., Wash.*, 1929, **3**, 91)]. Each ml. of the reagent precipitates about 1·4 mg. of aluminium. If more than 2 ml. are required, it is advisable to dilute the liquid to 50–60 ml. The solution is neutralised with diluted ammonia, and then made just acid with dilute acetic acid, after which the beaker is covered with a watch glass, heated to about 70° C. for 15 minutes, and allowed to stand at room temperature overnight. The precipitate is filtered off with the aid of suction, washed with small quantities of warm water, and dissolved in about 10 ml. of hot dilute (4 : 1) hydrochloric acid, and the solution is cooled and slowly titrated with 0·1 *N* bromine (bromide-bromate) solution, indigo carmine being used as indicator, and an excess of 0·5 to 1 ml. of bromine solution added. The exact excess is determined by adding potassium iodide and titrating with thiosulphate (starch as indicator): 1 ml. of 0·1 *N* bromine ≡ 0·000255 g. of aluminium. Sodium hydroxide solution should be kept in a bottle, the inner surface of which has been waxed.

The results of test analyses of various materials to which known amounts of aluminium had been added, gave results agreeing closely with the amounts taken. Under the conditions described, titanium, bismuth, tin and lead are the only common metals likely to be precipitated simultaneously with aluminium and iron phosphates. Titanium and bismuth are completely removed with the iron when this is separated as basic acetate. Tin and lead may be dissolved with the aluminium in dilute sodium hydroxide solution. Tin is not precipitated with 8-hydroxyquinoline in weakly acid solution. Lead gives a purple-brown precipitate which is much less insoluble than the greenish-yellow aluminium compound, but if the lead is present in much larger amount than aluminium, it must be removed by means of hydrogen sulphide before precipitating the mixed phosphates.

ACTION OF FOOD ON ALUMINIUM VESSELS.—The figures given by various workers for the amount of metal taken up by food from aluminium vessels vary considerably under different conditions. Thus the action of acids, when present in foods, appears to be much less than that of the pure acids alone.

In some experiments made for this Report, mutton broth containing mixed vegetables was cooked in an aluminium pan, and, after being sampled, was allowed to remain in the pan and re-heated on successive days. A similar mixture was cooked in an enamelled pan as a control. The results were as follows:

	Aluminium in broth p.p.m.
Cooked in enamelled pan ..	1·13
Cooked in aluminium pan—	
(i) Immediately after cooking	7·0
(ii) After 24 hours	10·6
(iii) After 48 hours	11·5

Several authors have drawn attention to the fact that corrosion of aluminium vessels becomes less during prolonged use and tends to reach a minimum, owing apparently to the formation of a resistant oxide coating. A process is, in fact, in operation for increasing this oxide coating to a thickness of 0·01 to 0·04 mm. by anodic oxidation (Elssner, *Chem.-Ztg.*, 1935, **59**, 213, 215).

The purity of the metal has some influence on its liability to corrosion. Commercial aluminium of 99·5 per cent. purity is more resistant than the aluminium formerly produced, which contained considerable amounts of iron and silicon.

BEHAVIOUR OF ALUMINIUM IN THE BODY.—The state in which aluminium may exist in the stomach contents probably varies with different conditions. It may be concluded that a considerable proportion of the aluminium taken into the stomach is soluble. The diffusibility of aluminium salts into the blood through the wall of the digestive tract appears to vary considerably with the circumstances. With regard to the effect on the digestive tract, a consideration of the recorded results indicates that, in reasonable doses, aluminium compounds do not make the normal person obviously ill within a period of weeks or months. The results of injection experiments cannot be deduced as evidence of toxicity when the substances in question are taken by the mouth. The general conclusion reached in the Report is that there is no convincing evidence that aluminium, in the amounts in which it is likely to be consumed as a result of using aluminium utensils, has a harmful effect upon the ordinary consumer. It is possible that there may be individuals who are susceptible to even such small doses of aluminium as may be derived from aluminium utensils, but evidence of this is inconclusive.

The Report concludes with an alphabetical list of 292 references.

Trinidad and Tobago

ADMINISTRATION REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1934

IN his Annual Report the Government Analyst (Mr. H. S. Shrewsbury) states that the work undertaken for the various departments of Government involved the examination of 4074 samples, 1497 of which consisted of foods.

"PHALKA GHEE."—A sample sold as "ghee," required by the Food and Drugs Ordinance to consist of pure butter-fat, was found to consist of an inferior vegetable fat known as "Phalka ghee" (meaning vegetable butter, and an obvious misnomer). So-called "Phalka ghee" is obtained from the seeds of various *Bassia* species, and is itself frequently adulterated with fats other than *Bassia*, such as coconut, arachis, cottonseed, safflower, sesame and niger seed oils; mahua, salvadora and castor oil are also sometimes used as adulterants, the last three being considered injurious.

ADULTERANTS OF COFFEE.—Of 157 samples of coffee, 24 were adulterated, the adulterants being burnt sugar, roasted pigeon peas and split pigeon peas (stated to be derived from varieties of the same plant); sometimes all three adulterants were present.

CAMPAIGN AGAINST VAMPIRE BATS.—The Department was able to assist the Medical Department in their campaign against vampire bats, considered to be the carriers of paralytic rabies in man and beast. The haunts of these bats are partly discovered by means of the excrement left therein; the excrement of vampire bats contains blood, very largely digested. The detection of blood therein serves to distinguish the excrement of vampire bats from that of all other species. It was for this purpose that 16 specimens of bat excrement were submitted by the Acting Medical Inspector of Health. Some of these were found to contain blood, proving the presence of vampire bats in the particular haunts from which the specimens were taken. It is useful to be able to detect the presence of vampire bats as distinguished from that of other species of bats, because whilst there is some hope of exterminating such a peculiar species as the vampire, and thus terminating the disease of paralytic rabies, it is impossible to exterminate all species of bats, and efforts made in this direction, instead of concentrating on the vampire, simply delay the time when the Island may possibly be completely rid of paralytic rabies. It has always been a very difficult matter to exterminate even a single species of animal.

Georgia Experiment Station

FORTY-SEVENTH ANNUAL REPORT, 1934–1935

The Report of the Director of the Station for the year 1934–1935 gives a survey of all the agricultural research work carried out in the State of Georgia, including the co-operative research with State and Federal agencies. Subjects investigated by the Chemistry Department include the following:

Boron and Cotton Nutrition.—Cotton nutrition study, carried out in water culture, was designed to determine the influence of the source of nitrogen upon the boron requirements of the cotton plant. Although the results obtained were not conclusive, they did indicate that there is little difference in the boron requirements of this plant regardless of whether ammonium- or nitrate-nitrogen is used. The results indicate that cotton has a high requirement and a high tolerance for boron, but that growing conditions have considerable influence on its effects on the plant. The results of this experiment also emphasise the need for more exact control of conditions in studies of this type. Contrary to results reported by other investigators, the presence of boron in the culture medium, and its consequent absorption, did not reduce the absorption of either calcium or magnesium. Evidence obtained indicates that there is but little relation between the concentration of boron in the culture solution and the amount of boron absorbed by the plant.

Freezing Preservation of Fruits and Vegetables.—A study of the reaction of different types of plant tissue to freezing was made. Evidence was obtained which indicates that the age and structural form of tissue have great influence on the reaction to freezing. The indications are that the variations in the reaction of different tissues to the freezing process are largely physical. In addition to its connection with freezing-preservation of fruits and vegetables, this study has a direct bearing on the use of expressed saps in the metabolism studies of plants.

Utilisation of Pimiento* Waste.—The principal red pigment of the Perfection pimiento has been isolated and identified as capsanthin. Previous studies have shown that colour development in egg-yolks follows within a very few days after the introduction of pimientos into the feed of the hen. Later studies have shown that the colour-effect of the pimiento on the egg-yolk disappears very slowly after the removal of pimiento from the feed. The pigment also seems to disappear from the body tissues much more slowly than it is deposited. In feeding experiments in which quantities of 0·4 g. and 3·0 g. of Perfection pimiento per 90 g. of basal diet were given to hens, the vitamin *A* content ranged from 20 to 40 units per g. of yolk.

Pimientos and Milk.—Two Holstein cows were fed on a low vitamin *A* ration for three months and until symptoms of vitamin *A* deficiency were apparent. The ration was then supplemented with dried pimientos for three weeks, and the increase in the vitamin *A* content of the milk was determined. All samples were kept frozen for several months before the biological tests were made. The amount of vitamin *A* in the milk after the pimiento feeding was three-fold that of the pre-feeding period.

Vitamin G [B_2] in Pimientos.—The vitamin G content of pimientos is evidently low. Upon the highest level fed, namely, 1 g. of canned product per day, the rats failed to gain weight during an experimental period of five weeks.

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* In this country pimiento is understood to refer to allspice, and pimento to capsicum varieties.—Editor.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Composition of Commercial Dried Whey. W. L. Davies. (*J. Soc. Chem. Ind.*, 1935, **54**, 338–341T.)—Nineteen samples of dried wheys of good quality, ranging in colour from rich cream to dark brown, which had been stored for a number of years, were analysed in detail, with the following results:—Moisture varied from 3·1 to 11·7 per cent., including at least 0·3 to 8·2 per cent. of "free" or hygroscopic moisture; ethereal extract was nil to 2·01 per cent.; ash was 7·03 to 8·37 per cent. on the dried whey, the chloride-content averaging for 15 samples 2·28 per cent., giving a saline taste to the whey, and in most cases affording means of identifying dried whey from dried skim or whole milk. The amounts of calcium and phosphorus were found to vary, and increased amounts appear in whey as the colour darkens. The average crude protein-content (N × 6·38) of 18 samples was 12·5 per cent., so that there does not appear to be any appreciable loss of nitrogen during drying. The true protein varied from 53·8 to 71·6 per cent. of the crude protein, which corresponds with a higher amount of non-protein nitrogen than is to be expected from the normal nitrogen distribution in milk, perhaps owing to partial hydrolysis of the soluble protein in acid whey during heating and drying. Usually the amount of protein rendered insoluble during drying was, roughly, half the true protein. Titratable acidity varied, as a rule, between 1·7 and 3·3 per cent. (as lactic acid), averaging 2·38 per cent.

D. G. H.

Nitrogen Distribution and Carbohydrate Partition in Philippine Rice Bran. J. Marañon and L. Cosme. (*Philippine J. Sci.*, 1935, **57**, 289–294.)—A high-grade rice bran known locally as "tikitiki" or "darak," obtained immediately after milling from a Manila mill, was found to have the following percentage composition:—Moisture, 11·65; fat (ethereal extract), 19·81; protein (nitrogen, 2·26 per cent.), 12·50; ash, 10·41; crude fibre, 6·32; and carbohydrates (by difference), 39·31. Nitrogen distribution was then determined; non-protein nitrogen by the method of Puchner, Leavenworth and Vickery (ANALYST, 1930, **55**, 406); protein nitrogen according to Stutzer's method (Leach and Winter, *Food Inspection and Analysis*, 4th Ed.); water-soluble nitrogen and free amino acid nitrogen by Van Slyke's method (*J. Biol. Chem.*, 1912, **12**, 275). The nitrogen partition after acid hydrolysis was carried out according to Jodidi and Moulton's procedure (*J. Amer. Chem. Soc.*, 1919, **41**, 1526). Calculated on the basis of total nitrogen on the moisture-free sample containing 2·264 per cent. nitrogen, the percentage proportions of nitrogen found were:—Non-protein, 11·44; protein, 88·56 per cent. The percentage distribution of the non-protein nitrogen was: acid amide, 1·68; humin, 0·93; basic, 1·37; and non-basic, 7·46; and that of the protein nitrogen, acid amide, 7·68; humin, 2·43; basic, 15·02; and non-basic, 63·43. The water-soluble nitrogen was 19·52 per cent. After acid hydrolysis the nitrogen distribution, calculated as before, was found to be: acid amide, 9·36; humin, 3·36; basic, 16·39; and non-basic, 70·89 per cent. The nitrogenous substances in rice bran thus consist mostly of protein, which is composed largely of non-basic nitrogen. Carbohydrate distribution (calculated on a basis of total carbohydrate on the moisture-free sample containing 51·65 per cent. total carbohydrates, including fibre) was as follows:—Reducing sugars, 0·87; non-reducing sugars, 11·66; starch, 46·76; dextrin, 1·01; hemicellulose, 1·61; pentosans, 17·58; crude fibre, 13·85; gums, 5·64; and undetermined, 1·02 per cent.

D. G. H.

Rate of Formation of Fully-saturated Glycerides during Hydrogenation of Different Natural Fats. T. P. Hilditch and H. Paul. (*J. Soc. Chem. Ind.*, 1935, **54**, 336–338T.)—Of the 6 fats studied, rape seed, olive and cottonseed oils conform closely, on the whole, to the "even-distribution" type of mixed glyceride, and this group would also include the Cape Palmas palm oil, whereas the Belgian Congo palm oil is less homogeneously built with a probably more complex configuration of the mixed glycerides, and the pig-back fat represents a somewhat different type. The proportions of (*a*) total saturated acids (per cent. mol.), and (*b*) palmitic acid (per cent. mol.) in the fats were as follows:—Rape seed oil (*a*) 3, (*b*) 2; olive, (*a*) 14, (*b*) 12; cottonseed (*a*) 27, (*b*) 25; pig-back fat, (*a*) 44, (*b*) 30; Cape Palmas palm oil, (*a*) 41, (*b*) 36; and Belgian palm oil, (*a*) 50, (*b*) 45. The hydrogenation data, reproduced on a curve, show that for a given total content of saturated acids, hydrogenated rape oil has the highest proportion of completely saturated triglycerides, followed in descending order by hydrogenated olive, cottonseed, pig-back fat and the two palm oils. On comparing the proportion of fully-saturated acids which have actually been produced from unsaturated acids present in the original fat, using as abscissae the molar amounts of saturated acids calculated as a percentage of the total unsaturated acids in the original fat, it will be found that the order of the curves is the exact opposite of the first picture, the Belgian Congo palm oil yielding the highest proportion of fully-saturated glycerides for a given degree of partial hydrogenation. The pig-back fat, with a content of palmitic acid somewhat less than that in the Cape Palmas palm oil, is quite out of line with the vegetable fat series. If, however, the data for this fat are plotted as fully-saturated glycerides in the hydrogenated fats against the total C_{18} acids present in the original fats, a curve results which falls exactly into position with that of the vegetable series, confirming the view in favour of the hypothesis that the palmito-stearo-glycerides of animal depôt fats have been produced as the result of partial reduction *in situ* of pre-formed palmito-oleo-glycerides.

D. G. H.

Oil of *Cassia absus*. Z. Ahmad. (*Z. Unters. Lebensm.*, 1935, **70**, 166–169.)—The seed-kernels of *C. absus* (Linn.) are largely applied in India as a household remedy in cases of eye trouble. The whole seeds yield 4 per cent. of dark green oil, and the kernels 6 per cent. of golden-yellow oil. The constants for the whole seed (kernel) oil are: sp.gr. at 26° C., 0·9276 (0·9284); n^{20}, 1·4840 (1·4735); saponification value, 190·4 (185·6); iodine value (Wijs), 130·5 (125·7); acetyl value, 12·0 (10·8); acid value, 2·5 (1·4); unsaponifiable matter, 8·4 (4·8) per cent. The fatty acids of the whole seed oil have: mean molecular equivalent, 282·4;

iodine value, 129·2; saturated acids 19·0, and unsaturated acids 81·0 per cent. The probable percentage composition of this oil is: oleic acid, 16·32; linolic, 47·32; linolenic, 0·41; hydroxy-acids, 0·75; palmitic, 6·28; stearic, 8·10; lignoceric acid, 0·82; unsaponifiable matter, 8·40; glycerol, 10·40; undetermined, 1·20. The oil contains a saturated hydrocarbon in small amount, and 0·11 per cent. of phytosterol. T. H. P.

Composition of Szegeder Edelsüss Paprika Meal Products. I. Horváth. (*Z. Unters. Lebensm.*, 1935, **70**, 195–201.)—This material, which is the most important Hungarian spice, consists of a ground mixture of the ripe, red fruits of paprika with a proportion (varying) of the fruit husks and seeds which have been purified by washing and mechanical treatment. The colour varies from dark red for products containing much seed to pale red for those with relatively little seed. The mean percentage compositions of a number of deep red, bright red, and pale red samples were found to be:—Loss at 100° C., 8·2, 7·8, 10·7; ash, 5·32, 5·74, 6·06; sand, 0·27, 0·24, 0·17; ether extract, 15·77, 13·34, 12·25; petroleum spirit extract, 14·37, 12·45, 11·28; nitrogen, 2·45, 2·39, 2·37; crude protein, 15·29, 14·97, 14·81; sugar as invert sugar, before inversion, 12·51, 13·71, 14·84; ditto, after inversion, 13·48, 14·53, 15·57; crude fibre, 23·16, 23·86, 23·16; essential oil, 0·085, 0·135, 0·113. The methods of analysis are briefly outlined. T. H. P.

Nicotine-content of Tobacco Smoke. C. O. Jensen and D. E. Haley. (*J. Agric. Res.*, 1935, **51**, 267–276.)—Methods of determination of nicotine are reviewed, and a modification of Chapin's procedure (*U.S. Dept. Agr., Bur. Animal Indus. Bull.*, 1911, 133) is recommended. Preliminary experiments showed that with solutions containing less than 0·02 per cent. of pyridine there is little interference with the method as normally applied to cigarette smoke, and that ammonia also is without influence on the results. An apparatus is described for "smoking" the cigarettes, in which the sample is held in one end of a calcium chloride tube, the other being connected through 4 absorption vessels in series with a vacuum pump with a slowly-rotating valve. The cigarettes were stored for 2 weeks under conditions of standard humidity, and 5 were then weighed and smoked with puffs lasting 1·6 seconds, with intervals of 6·1 seconds between puffs; 20 ml. of air passed through the cigarette at each puff into the absorbing vessels, each of which contained 12·5 ml. of chloroform and 12·5 ml. of 0·1 *N* sulphuric acid. The cigarette-holder and the vessels were washed with chloroform and water, and the aqueous layer from the bulked washings and absorption solutions (containing nicotine sulphate) was steam-distilled in the presence of 35 ml. of sodium hydroxide solution, the distillate, which amounted eventually to 500 ml., being collected in water and acidified with 15 ml. of 25 per cent. hydrochloric acid. The nicotine was then precipitated with 5 ml. of 12 per cent. silicotungstic acid, and on the next day it was filtered through a weighed Gooch crucible which was subsequently heated at 125° C. for 3 hours and re-weighed. Experiments with tobaccos containing 0 to 24·44 per cent. of moisture showed that the percentage of nicotine in the smoke, compared with that present in the tobacco (respective values, 42·4 and 21·2 per cent.), varies inversely as the moisture-content. A decrease in the strength of the puff (corresponding with the passage of 16 ml. of air through the cigarette) decreased the percentage of nicotine in the smoke. Studies of the amount of nicotine in the unsmoked butt were made by coating this portion with paraffin wax and inserting it in the warm glass holder, so that, on cooling, the wax made an air-tight joint. Cigarettes 7 cm. long (moisture, 11·1, and nicotine, 2·17 per cent.) were smoked until butts 1 and 3 cm. long remained, and the nicotine in the butt was calculated from the formula $100\ (5{\cdot}7\ F-A)/5{\cdot}7\ F$, where A is the amount of nicotine in the smoke per cigarette whose dry weight equals 1 g., and F is the fraction of the cigarette smoked; values found were 22 and 60 per cent., respectively. Investigations on the "side-stream" smoke were made by placing the cigarette loosely in an opening (slightly larger in diameter than the cigarette) in a bulb, the smoke being drawn out continuously through an opening in the opposite side of the bulb into the absorbing vessels. The percentages of nicotine in the main and side streams (compared with the total nicotine in the tobacco) were, respectively, 26·3 and 31·8 for a moisture-content of 11·13 per cent., and 42·4 and 28·6 for bone-dry tobacco. This apparent contradiction of some of the results given above may be explained partly by the fact that dry cigarettes burn more rapidly than moist tobacco, so that in the former case there is more distillation and less destruction of the nicotine. J. G.

Occurrence of Hydrogen Sulphide in Tobacco Smoke. A. Wenusch. (*Z. Unters. Lebensm.*, 1935, **70**, 201–204.)—The proportion of hydrogen sulphide in tobacco smoke depends not only on the nature of the tobacco, but also on its method of preparation and on the way it is smoked. Cigarettes of oriental tobacco usually yield less hydrogen sulphide than cigars, and the sulphide increases in quantity with the rate of smoking. With intermittent smoking, a sample of cigars gave 0·019 per cent., and Memphis cigarettes 0·007 per cent. of hydrogen sulphide. Evidence is cited in disagreement with Vogel's view that the sulphide is derived from sulphuric acid pre-existing in the tobacco (*Dingler's Polytechn. J.*, 1858, **148**, 231). A more probable source is the protein of the tobacco. The hydrogen sulphide contributes to the aroma of the smoke, but is insufficient in amount to have toxicological importance. T. H. P.

Biochemical

Carcinogenic Hydrocarbons and their Relationship to the Sterols. J. W. Cook. (*Chem. Weekblad*, 1935, **32**, 563–566.)—Earlier work on the carcinogenic effects of coal tar and similar products is reviewed; the results indicate that the active substance is a hydrocarbon, and is responsible for the bands 400·0, 418·0 and 440·0$m\mu$, which are common to the fluorescence spectra of many carcinogenic mixtures. The strong fluorescence of anthracene suggested the synthesis of homologues and benzologues of 1·2-benzanthracene, in the hope of finding a compound which would reproduce these spectral characteristics, and the results obtained are summarised in the present paper. *Tetracylic and Pentacylic Aromatic Hydrocarbons.*—Of the 15 hydrocarbons with 5 condensed benzene rings which are theoretically possible, 12 have been examined, but only 1.2.5.6-dibenzanthracene and 1.2-benzopyrene were found to have any pronounced activity. Of the

6 possible hydrocarbons with 4 condensed benzene rings, chrysene and 3.4-benzophenanthrene were slightly active, the latter being the simplest carcinogenic chemical compound known, and the only one not related to 1.2-benzanthracene. *Derivatives and Homologues of* 1.2-*Benzanthracene.*—Activity is usually evident when there are substituents at positions 5 or 6, or both, but rarely in other cases; substitution at position 5 is the more effective in inducing carcinogenic activity. Data given in support of these generalisations show the numbers of epitheliomas and papillomas produced in a given time in mice for the various derivatives. With the exception of 5.6-*cyclo*penteno-1.2-benzanthracene, none of the numerous simple derivatives and homologues of 1.2.5.6-dibenzanthracene examined had a greater activity than the parent substance, substitution in the *meso*-position or reduction of the ring-system being particularly effective in reducing the carcinogenic power. *Coal-tar Carcinogens.*—The fluorescence spectrum was used as a method of control in the fractional distillation of 2 tons of coal-tar pitch, and in this way it was possible to select fractions which, after extraction with solvents and crystallisation of the picrates, yielded a few g. of a substance which was identified by synthesis as 1.2-benzopyrene. Since both the synthetic and isolated products had the characteristic fluorescence spectra associated with carcinogenic materials (cf. *supra*), and produced tumours in about half the time required by 1.2.5.6-dibenzanthracene, it is assumed that 1.2-benzopyrene is the principal, but not necessarily the only carcinogenic substance in coal tar. *Carcinogens derived from the Bile Acids.*—The introduction of the Rosenheim-King formulation for the bile acids (1932) suggested a structural relationship with the carcinogenic hydrocarbons, because the side-chain of the sterol-bile acid molecule is in such a position that cyclisation leads to a hydrogenated 1.2-benzanthracene ring-system. Thus, oxidation and then reduction of de-oxycholic acid yields 12-ketocholanic acid, which is converted into dehydro-norcholene by thermal dehydration and decarboxylation. This, in turn, may be dehydrogenated, in the presence of selenium, to form the aromatic hydrocarbon methylcholanthrene, a 5.6-substituted derivative of 1.2-benzanthracene and the most active carcinogen yet encountered; thus, a 0·3 per cent. solution in benzene produced tumours in the skin of mice after 75 days. Recent work on the structure of the hormones has shown them to be biological degradation products of cholesterol differing in the degree of hydrogenation of the ring-system, and it is therefore inferred that some enzymic factor in the body may be capable of effecting dehydrogenation of the sterol ring-system. Excessive activity of this factor may possibly contribute to the production of carcinogens *in vivo.* J. G.

Titration of Fluorine in Biological Materials. E. W. Scott and A. L. Henne. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 299–300.)—*Ashing.*—To samples of tissues (*e.g.* heart, lungs, spleen, etc.), solid lime or lime water, as appropriate, is added, and the whole is well dried in a silica basin for several days at a "medium temperature." No lime addition is made with teeth or bones. The bulk of fat-containing samples is burned by inserting a wick and igniting while hot. The dried sample is ashed for 12 to 24 hours at 600° C. Teeth or bones require about 48 hours at 650–700° C. Fusion of sample (*e.g.* of liver) indicates insufficient lime addition. The residue is finely ground in a mortar. *Separation of Fluorine.*—The ash (1 g.) is decomposed with perchloric acid and the fluorine is distilled off as hydrofluosilicic acid by the method of Willard and Winter (*Ind. Eng. Chem., Anal. Ed.*, **1933**, **5**, 7, Abst., ANALYST, **1933**, **58**, **242**). *Titration of Fluorine.*—The volumetric method proposed by Willard and Winter was not found satisfactory, and the following method was adopted: To the distillate, a few drops of 0·04 per cent. phenol red solution are added; the solution is neutralised with sodium hydroxide and evaporated to a volume of 2 to 3 ml., additions of 0·01 *N* perchloric acid being made meanwhile from time to time to maintain neutrality. Two drops of a saturated alcoholic solution of methyl red and 10 drops of 0·04 per cent. aqueous bromocresol green solution (exactly neutralised with sodium hydroxide) are added. The liquid is titrated at 80° C. to the "maximum red colour" with cerous nitrate solution (1 ml. ≡ 0·5 mg. of fluorine; method of standardisation not specified). When the amount of fluorine is less than 0·2 mg., thorium nitrate solution (1 ml. ≡ 0·1 mg. of fluorine) may be substituted for the cerous nitrate, the same mixed indicator being used; it was found necessary to make a deduction of 0·02 mg. of fluorine in the determination of these small amounts. In test experiments the ash was divided into two parts, to one of which was added a known amount of calcium fluoride. Determination of fluorine in the two portions gave differences corresponding closely with the added calcium fluoride. S. G. C.

Metabolism of the Phospholipids. The Passage of Elaidic Acid into Tissue Phospholipids. R. G. Sinclair. (*J. Biol. Chem.*, 1935, **111**, 515–526.)—Elaidic acid may comprise one-third of the total fatty acids in the phospholipids of the liver and skeletal muscles of rats which have been raised on a diet rich in elaidin. When adult rats which have been raised on ordinary diets are fed with elaidin, elaidic acid may replace 25 to 30 per cent. of the natural fatty acids, chiefly the fully-saturated acids. The rate of appearance of elaidic acid in, and disappearance from, the phospholipids is rapid in the liver and slow in muscle. This process is practically complete in the liver in one day, but many days are necessary for the muscle. From the factors governing both the degree of unsaturation of the phospholipids and the rate of turnover of elaidic acid it is suggested that at least two classes of phospholipids exist. One class consists of the more highly unsaturated phospholipids, and is concerned in the essential make-up of the cell; the other class consists of the less unsaturated compounds, and is an intermediate product in fat metabolism. Both classes are present in the liver, but the non-metabolic type is the important one in skeletal muscle. S. G. S.

Use of a Closed Titration Flask in the Bromometric Determination of Magnesium with 8-Hydroxyquinoline in Tissues and Urine. D. M. Greenberg, C. Anderson and E. V. Tufts. (*J. Biol. Chem.*, **1935**, **111**, 561–565.)—The magnesium precipitate is dissolved in strong hydrochloric acid and washed into a suction flask whose side tube is plugged with cotton wool. The mouth of the flask is then closed with a paraffined cork stopper which carries a funnel having a stem long enough to reach below the level of the liquid in the flask. Bromination is carried out in this flask, then potassium iodide is added, and the liberated iodine titrated in the same vessel. In the determination of magnesium in urine, 10 ml.

are adjusted to *p*H 5·0–5·5, heated with 5 ml. of 4·5 per cent. potassium oxalate and diluted to 50 ml. After filtration an aliquot portion is used for the determination. If the urine contains protein, this must be removed by treatment with trichloroacetic acid and the filtrate used for the oxalate precipitation. Tissues should be dried and ignited, and the ash dissolved in *N* hydrochloric acid and treated in a similar manner. Iron may be removed by precipitation with hydroxyquinoline at *p*H 5·0 (Alten, Wieland and Kurmies, *Z. angew. Chem.*, 1933, **46**, 697), after which the magnesium is precipitated by the method previously described. (Greenberg and Mackey, *J. Biol. Chem.*, 1932, **96**, 419; ANALYST, 1932, **57**, 730.) S. G. S.

New Method for the Determination of Minute Amounts of Lead in Urine. J. R. Ross and C. C. Lucas. (*J. Biol. Chem.*, 1935, **111**, 285–297.)—The urine (100 ml. or more) is adjusted to *p*H 4·5 in a suitable glass-stoppered tube by the addition, in drops, of glacial acetic acid. Approximately 0·5 g. of powdered ammonium oxalate is then added and mixed with the solution. This is followed by 2 ml. of 10 per cent. calcium chloride solution, again with thorough mixing. The lead is, in this way, completely precipitated by entrainment with the calcium oxalate precipitate. After the mixture has stood for at least 20 minutes with occasional shaking, the open end of the tube is covered with a cigarette paper held in place by a rubber band and the tube is centrifuged. The supernatant liquid is discarded, and the precipitate is washed with about 20 ml. of double-distilled water containing a few drops of saturated ammonium oxalate solution. The precipitate of calcium oxalate and uric acid is broken up with a glass rod, and the whole is again centrifuged. After the wash-water has been decanted, the tube is inverted and allowed to drain on filter-paper. This removes most of the phosphates, which otherwise would interfere later in the procedure. The precipitate is next treated with 2 ml. of perchloric acid and 2 drops of 30 per cent. hydrogen peroxide, and the mixture is heated for at least 20 minutes. To the hot mixture 3 drops of strong hydrogen peroxide are added cautiously, and the heating is continued for 3 minutes. After cooling, 5 ml. or more of double-distilled water are added, followed by 3 ml. of 10 per cent. citric acid solution, to prevent the precipitation of traces of phosphates which may be present. The solution is then made just alkaline by the careful addition of concentrated ammonium hydroxide solution, bromothymol blue being used as the indicator. If it is made too alkaline a precipitate will form, and this must be dissolved in citric acid. The whole, or an aliquot part, of the solution is transferred to a 50-ml. separating funnel, and 4 drops of 20 per cent. sodium cyanide solution are added. The volume at this point should be about 20 ml. The mixture is then shaken vigorously with about 1 ml. of purified dithizone solution. The cherry-red solution of lead dithizone in carbon tetrachloride is drawn off, and the extraction is repeated with 1-ml. or diminishing portions of the dithizone solution until no further red colour appears. The mixed red dithizone solutions are washed with 10 ml. of 0·5 per cent. ammonium hydroxide solution containing 2 or 3 drops of sodium cyanide solution, made up to a definite volume with carbon tetrachloride, and compared with a standard lead solution in a colorimeter. It is sometimes preferable to shake the red solution with dilute (1 : 3) hydrochloric acid and compare the green colour so formed. The purified dithizone solution is prepared by dissolving about 4 mg. of commercial dithizone in 25 ml. of carbon tetrachloride. This is extracted three times with 25 ml. of 0·5 per cent. ammonium hydroxide. The carbon tetrachloride layer is rejected and the aqueous layer is neutralised to litmus with $N/1$ hydrochloric acid solution. This is then extracted with 15-ml. portions of carbon tetrachloride, which are united, diluted to 100 ml. and kept in a refrigerator. This solution will last for 3 days. The recovery of lead added to urine was such that the accuracy appears to be ± 0·004 mg. of lead for amounts up to 0·10 mg. Normal urine was found to contain 0·05 mg. per l. for adults and 0·06 mg. per l. for children. Urine from lead workers contained up to 0·64 mg. per l. S. G. S.

Determination of the Pectolytic Power of Filtration Enzymes. A. Mehlitz and H. Maass. (*Z. Unters. Lebensm.*, 1935, **70**, 180–186.)—The clearing of fruit juices and sweet musts depends fundamentally on the removal of the pectin. This may be effected spontaneously by means of pectase present in the juice, or, very incompletely, by treatment with tannin and gelatin, the precipitate formed then adsorbing the pectin. Both of these methods are surpassed by Mehlitz's process, which makes use of so-called filtration enzyme preparations, these hydrolysing the pectin to a finely dispersed form and converting this into monogalacturonic acid in a state of true solution. The method previously given for determining the pectolytic power of these enzyme preparations (*ibid.*, 1934 **68**, 96) has certain disadvantages, and is now replaced by the following procedure: 200 ml. of a pectin solution yielding about 2 (1·7 to 2·3) g. of calcium pectate, and having *p*H 3·6, are mixed for 5 minutes with 1 g. of the enzyme preparation in a 250-ml. flask with a ground stopper. The flask is kept for 15 hours in a thermostat at 37° to 38° C., after which 10 ml. of 40 per cent. (vol.) formaldehyde solution are added, and the stopper is at once replaced. The liquid is cooled and filtered through a pleated paper, 25 ml. of the filtrate being transferred to a 250-ml. measuring flask and made up, with frequent swirling, to the neck of the flask, with water at 80° C. After being cooled, the solution is made up to 250 ml. and mixed. Ten ml. of the liquid are mixed with 80 ml. of water and 10 ml. of N sodium hydroxide in a 400-ml. wide-form Jena beaker, which is covered, and left at least 7 hours, 50 ml. of N acetic acid and 50 ml. of 2 N calcium chloride solution being then added. The whole is boiled for about 3 minutes, and the calcium pectate precipitate is collected on a weighed filter (Schleicher and Schüll, No. 589, 11 cm. diameter), and washed with hot water until it gives no reaction with silver nitrate. The paper and precipitate are dried at 105° C. until constant in weight (at least 6 hours). The weight of the precipitate is multiplied by 1·05 to correct for dilution of the solution with the formaldehyde, and the weight thus obtained is subtracted from that of the calcium pectate given by 10 ml. of the original, unfermented solution. Multiplication of this remainder by 5 gives the pectolytic activity in Mehlitz units. T. H. P.

Method for the Direct and Quantitative Study of Amyloclastic Activity of Amylases. M. L. Caldwell and F. C. Hildebrand. (*J. Biol. Chem.*, 1935, **111**, 411–420.)—The method is based upon the direct determination of residual starch or amylose at any stage in its hydrolysis, and depends upon quantitative precipitation, free from dextrins and maltose, by ethyl alcohol. To the solution of starch or amylose dispersion, sufficient alcohol is added to give a final concentration of 55 per cent. by volume. The mixture is stirred vigorously by hand, and a flocculent white precipitate is formed fairly quickly. This is allowed to settle, and the supernatant liquid is decanted through a Gooch crucible containing a thin mat of asbestos and half filled with fluffy asbestos, which (with the crucible) has previously been heated to constant weight in a muffle-furnace. The precipitate is washed by decantation, twice with 55 per cent. and twice with 70 per cent. alcohol. The washed precipitate is finally transferred to the crucible with a jet of 96 per cent. alcohol and washed with a mixture of equal volumes of 96 per cent. alcohol and ether. The crucible is then dried to constant weight at 105° C., cooled and weighed. The crucible may be used again, if, after each determination, it is heated at a low red heat for 3 hours. S. G. S.

Remarks concerning the New Colour Reaction of Vitamin *A*. E. Rosenthal and J. Erdélyi. (*Biochem. J.*, 1935, 29, 2112–2113.)—In the colour test for vitamin *A*, which was first described by these authors in 1934 (*Biochem. J.*, 1934, **28**, 41; ANALYST, 1934, **59**, 562), the use of alcohol-free chloroform is recommended. With the use of guaiacol, as suggested, it is unnecessary to warm the reaction mixture, as the colour produced in the cold is quite stable and can be compared with that of a freshly-prepared dilute solution of potassium permanganate. Warming the reaction mixture is necessary only if it is desired to demonstrate vitamin *A* in the presence of carotene. S. G. S.

Observations on the Estimation of Ascorbic Acid by Titration. E. W. McHenry and M. Graham. (*Biochem. J.*, 1935, 29, 2013–2019.)—The following modifications in the titration of ascorbic acid by 2 : 6-dichlorophenolindophenol were used. The indicator was prepared in a phosphate buffer solution at *p*H 7·2. A secondary standard, consisting of a slightly acid solution of ferrous ammonium sulphate, was used, which was kept for 6 months without loss in an atmosphere of nitrogen in an automatic burette. This was standardised against ascorbic acid through the medium of the indicator solution. In order to avoid the error caused by the reduction of the indicator by acid, the indicator solution was diluted with 15 to 20 volumes of water just prior to the titration. It was found that, with solid foods, at least three extractions with trichloroacetic acid were necessary, but that a 3 per cent. acid solution gave less destruction than the usual 5 per cent. The addition of a few drops of potassium cyanide solution during extraction also stabilised the ascorbic acid present. An increase in the volume of the extraction solution was found to give increased accuracy. Where the plant pigment was insoluble in chloroform it was found that interference from this source was avoided if this solvent was added to the titration flask. The tip of the burette was lowered into the chloroform, and the aqueous layer was stirred by bubbling carbon dioxide through it without disturbing the chloroform layer. Where the plant pigment was soluble in chloroform it was found possible to extract it with butyl or amyl alcohol. This was then washed with water, and the aqueous solution was added to the acid extract. The loss by this method was insignificant.

Vegetable tissues generally contain appreciable amounts of reversibly oxidised ascorbic acid, for they do not appear to possess a mechanism which prevents the aerobic oxidation of ascorbic acid. Some of the vegetables examined showed an increased titration value after heating or after acid hydrolysis. This is believed to be due to the liberation of ascorbic acid from a compound which is soluble in water, but insoluble in trichloroacetic acid. S. G. S.

Effect of Feeding Cacao Shell to Cows on the Vitamin *D* content of Butter (Milk). S. K. Kon and K. M. Henry. (*Biochem. J.*, **1935, 29, 2051–2056.**)—Cacao shell was found to contain 35 international units of vitamin *D* per g., when determined by curative and protective experiments on rats. This agrees well with the results of Knapp and Coward (ANALYST, **1934, 59, 474**), who found 28 units per g. The fat of cacao shell contains about 300 units of vitamin *D* per g. The extractable fat accounts for about 40 per cent. of the total activity of the shell. By feeding to two Shorthorn cows, under winter-stall feeding conditions, 2 lbs. of cacao shell daily for a month, the vitamin *D* content of their butter-fat was raised from the winter to the summer level, without any untoward effect on the cows. S. G. S.

Water

Determination of Lead in Potable Waters. J. F. Reith and J. de Beus. (*Z. anal. Chem.*, 1935, **103**, 13–27).—The colorimetric determination of lead as sulphide was re-investigated, the authors offering a choice of three procedures. The sample is prepared by addition of 5 ml. of 4 *N* hydrochloric acid per l. to dissolve any deposit which may contain lead. The acid is allowed to act for 15 minutes.

Procedure A, for water containing less than 10 mg. of iron per l., and either colourless or hardly coloured by organic matter: 80 ml. of prepared water are treated in a Nessler tube with 4 drops of 10 per cent. potassium cyanide solution, 10 ml. of 20 per cent. Rochelle salt, and 10 ml. of 20 per cent. ammonium chloride solution in 2 *N* ammonia, with agitation after each addition. The colour, if any, is matched against a scale of tubes containing 0, 5, 10, etc., γ of lead, and treated with the same reagents and 2 drops of fresh sodium sulphide solution (10 g. of crystals dissolved in 25 ml. of water and made up to 100 ml. with glycerin. The solution should be free from thiosulphate, *i.e.* a few ml. of 5 *N* acetic acid treated with 10 drops of the sulphide solution should show no opalescence within 15 minutes). The tube containing no lead should be practically as colourless as distilled water. The unknown solution is then treated with 2 drops of sulphide solution, and the colour is again matched against that of a scale of tubes, if necessary after a preliminary determination. The standard lead solution contains 160 mg. of pure lead nitrate and 5 ml. of 5 *N* acetic acid per l. The determination should not take more than 10 minutes, after which time bleaching takes place. The colour in terms of γ of lead prior to addition of sulphide is subtracted from the last reading.

Procedure B, for water containing more than 10 mg. of iron per l., and showing a yellow tinge due to organic matter. To 100 ml. of prepared water are added

5 ml. of 5 per cent. ammonium persulphate solution; the water is boiled down to 50 ml., cooled to 50° C., and treated with 4 drops of cyanide, and 10 ml. of Rochelle salt solution. If the liquid is clear, 10 ml. of ammoniacal ammonium chloride solution are added after a few minutes, the water is cooled, transferred to a Nessler tube, and tested as under A. If, on the other hand, the liquid is not clear, it is filtered into the tube, the filter is washed 3 times with 5-ml. portions of water faintly acidified with hydrochloric acid; the filtrate is made up to 90 ml., and treated with 10 ml. of the ammonium chloride solution; it is then tested as before.

Procedure C. This comprises enrichment by adsorption on calcium carbonate, suitable for all practical cases, including highly ferruginous water. One l. of water (or a smaller quantity of prepared water supposed to yield 50 to 100 γ of lead) is treated in a flask with 5 ml. of cyanide solution, 3 drops of phenolphthalein indicator, and just enough 4 *N* caustic soda is added, drop by drop, to faint but permanent alkaline reaction. Precipitated pure calcium carbonate (0·5 g.) is added, the water is left for an hour with occasional agitation, and decanted, after 2 to 3 hours' settling, through a small Buchner funnel. The deposit is washed 4 times with 25-ml. portions of water containing a little sodium bicarbonate, and dissolved in hot hydrochloric acid (5 ml. of 4 *N* acid and 40 ml. of water). The solution is collected in a 300-ml. flask, and, with the washings, is made up to a volume of 150 ml. The liquid is treated with 5 ml. of the persulphate solution, and boiled down to 80 ml.; hydrazine hydrochloride (0·1 g.) is then added, and boiling is continued for some minutes until the liquid is quite colourless. It is cooled and transferred (or filtered if necessary) into a Nessler tube. The blank colour of the water is now ascertained by means of a scale of 3 tubes containing 0, 5, and 10γ of lead in 90 ml. of water, 10 ml. of ammonium chloride *plus* acetate (15 and 20 per cent.) solution, and 2 drops of the sulphide reagent. The unknown water is also treated with 10 ml. of chloride-acetate reagent (which should yield a liquid neutral to Congo red, otherwise more of the reagent is required). Two drops of the sulphide solution are added, and the resultant tint is matched as before. As a check, 10 ml. of 4 *N* hydrochloric acid are added to the tube after the comparison; the colour due to lead disappears after a few minutes, whilst any due to mercury, copper or bismuth remains.

W. R. S.

Agricultural

Composition of Crude Fibre. A. G. Norman. (*J. Agric. Sci.*, 1935, **25**, 529–540.)—Detailed analyses of the crude-fibre fraction from a wide range of agricultural materials showed that it consists almost entirely of cellulose and lignin, these two substances forming, on an average, 97 per cent. of the fraction. Comparison with the composition of the original material, however, indicated that the cellulose of the fibre (with the exception of bran) represented a recovery of 60 to 80 per cent., but that the proportion of lignin varied very much, and represented a recovery of 4 to 67 per cent., confirming the fact that the crude-fibre fraction does not represent any constant fraction of the plant constituents, and that the crude fibre from one material is not necessarily comparable with that from another. The composition of the fraction obtained by acid treatment indicated that this attacks the cellulose to only a limited extent, and the lignin slightly, whilst the subsequent alkali treatment appears to remove practically all the remaining hemicellulose and protein and a considerable quantity of lignin. It also largely, but not exclusively, removes the xylan of the cellulose. A discussion of the requirements of any method of assessing fibre emphasises the point that all lignin should be removed, and to achieve this the alkaline extraction must be dispensed with. Acid hydrolysis is suggested as a possible alternative empirical method, but a correction for protein would have to be introduced for all materials high in nitrogen and a determination of lignin made. D. G. H.

Organic

Determination of Free Primary and Secondary Alcohols in the presence of Tertiary Alcohols in Essential Oils by Acetylation in Pyridine. R. Delaby and S. Sabetay. (*Bull. Soc. Chim.*, 1935, 2, 1716–1724.)—A modification of the method of Radcliffe and Chadderton (*Perf. and Essent. Oil Rec.*, 1926, **17**, 352) has been devised in which acetic anhydride is used to replace phthalic anhydride. Under the conditions described, primary alcohols, primary amines, and phenols are quantitatively acetylated in less than an hour, and secondary alcohols almost quantitatively in about an hour, whilst tertiary alcohols and aldehydes react only with difficulty. The acetylating mixture (which keeps well) is prepared by mixing 1 part by weight or volume of acetic anhydride with 2 parts of anhydrous pyridine, previously heated beneath a reflux condenser with barium hydroxide and afterwards distilled. Five ml. of the acetylating mixture are usually employed, but less may be used, the essential condition being that there must always be two or three times the theoretical amount of acetic anhydride required. Two acetylation flasks of Pyrex glass are required, each provided with a ground-in reflux condenser about 1 m. long, and one is used for a blank determination. The flasks are heated by immersion in a boiling water-bath. The initial acidity of the sample must be determined, and an allowance must be made for any ethyl alcohol present. From 0·5 to 3 g. of the substance are heated for ½ to 1 hour in the acetylating flask with 5 ml. of the acetylating mixture, 50 ml. of water are introduced through the upper end of the condenser, and heating is continued for 15 minutes, with occasional shaking. When cold, the liquid is transferred to a beaker, the flask and condenser are rinsed out with water, and the liquid is titrated with $N/2$ alcoholic potash, phenolphthalein being used as indicator. The end-point is very sharp. The following are examples of results obtained by the method, the times given being the times of acetylation:—(i) Primary alcohols: benzyl alcohol (1 hour), 99 per cent.; geraniol (½ hour), 98·7 per cent.; *l*-citronellol (½ hour), 99·3 per cent. (ii) Secondary alcohols: menthol (½ hour), 97·6 per cent.; borneol (1 hour), 95·9 per cent.; cyclohexanol (½ hour), 88·1 per cent. (1 hour), 93 and 93·6 per cent. (iii) Tertiary alcohols: methylpropylbenzyl carbinol (1 hour), nil; linalol (½ hour), 1 per cent.; terpineol (½ hour), 2·3 per cent. (iv) Aldehydes: citronellal (½ hour), 4·7 per cent.; citral (½ hour), 5·7 per cent.; (1 hour), 7·9 per cent.; benzaldehyde (1 hour), nil. (v) Primary amine: methyl anthranilate (1 hour), 99·6 per cent. (vi) Essential oil: Geranium Bourbon (acid value 3·8) (1 hour), 38·6 per cent. of

geraniol. Breugnot applied the phthalic anhydride method (Radcliffe–Chadderton technique) to each of the essential oils examined by the authors and obtained results of the same order. A. O. J.

Use of Thiohydrazides as Reagents for Aldehydes. H. Wuyts and H. Wachsmuth. (*J. Pharm. Chim.*, 1935, **22**, 289–305.)—The reaction previously described (ANALYST, 1933, **58**, 481) is now applied to a number of aldehydic compounds of pharmaceutical interest, the three reagents used being *α*-phenyl-*β*-thiobenzoylhydrazine, *α*-*p*-bromophenyl-*β*-thiobenzoylhydrazine, and *α*-phenyl-*β*(thio-*α*-naphthoyl)-hydrazine. The compounds obtained by the condensation of these with formaldehyde, acetaldehyde, benzaldehyde, cinnamaldehyde, anisaldehyde, piperonaldehyde, dimethylaminobenzaldehyde, salicylaldehyde, vanillin and furfural are described and their melting-points given. Not only are such derivatives useful in the identification of aldehydes, but it is probable that the formation of certain of them may serve as the basis of a method of determining the aldehydes. T. H. P.

Component Fatty Acids of Glycerides of Partly Hydrogenated Rape Oil. T. P. Hilditch and H. Paul. (*J. Soc. Chem. Ind.*, 1935, **54**, 331–336T.)—Rape oil and the methyl esters prepared from its mixed fatty acids were progressively hydrogenated, and the component acids of the glycerides determined together with those of the partially hydrogenated methyl esters. Since the fatty acids of rape oil contain about equal proportions of unsaturated C_{18} (oleic and linolic) and C_{22} (erucic) acids, the ester fractionation analysis is complicated, lead erucate being only sparingly soluble in alcohol, and certain modifications of procedure are introduced. In the mixed esters hydrogenation of the linolates proceeds selectively as usual, and oleate is converted into stearate rather more readily than erucate into behenate, but in the glycerides the selectivity is less marked, owing perhaps to the configurational positions of the unsaturated radicals in combination in the glycerides. Examination of the fully-saturated glycerides produced during the progressive hydrogenation of rape oil showed no evidence of the presence of triglycerides or of trierucin. Rape oil conforms closely to the usual "even-distribution" rule characteristic of the glyceride structure of seed fats. The rape oil contained, in addition to about 6 per cent. of mixed palmito-oleo-(linoleo)-erucins, about 50 per cent. of di-C_{18}-erucin and about 44 per cent. of mono-C_{18}-dierucin (the C_{18} acid being either oleic or linolic). All possible configurations of *α*- and *β*-oleo-(linoleo)-dierucins and *α* and *β* erucodioleins (linolins) are probably present. D. G. H.

New B.S.I. Specification [for Asphaltic Compositions] and the Chemist. D. M. Wilson. (*Highways and Bridges*, 2nd Oct., 1935.)—B.S.S. No. 594 provides for the use of 3 alternative cements, *viz.*:—Asphaltic bitumen, refined lake asphalt (fluxed), and equal proportions of these. They differ widely in cost, but simple chemical analyses (*e.g.* solubility in carbon disulphide, ash-content and penetration tests) are available to show whether they meet the requirements. When, however, the asphalt cement has been manufactured into an asphalt mixture it is difficult to say for certain whether the specifications have been fulfilled, and tests are described to meet this necessity. It has been shown (*id.*, 4th Dec., 1934) that each bitumen or bitumen mixture has a characteristic colour value; the asphalt bitumens are, as a rule, darker than the bitumen in Trinidad Epuré, and the number of neutral tint units increases regularly with increasing powers of penetration. The hardening which bitumen undergoes when converted into asphalt was simulated by heating at 200° C. for a prolonged period, with and without "blowing" by a current of air, and the relationships between the penetration and colour values of the resulting products were then plotted. The curves show that in both cases (with Mexphalte and Fluxed Trinidad Epuré) the colour depends only on the degree of penetration, and is unchanged by ageing, and this conclusion was confirmed by tests on a sample from a road 9 years old. Colour values are best determined in the 0·5 cm. cell of the Lovibond Tintometer on 0·25 per cent. extracts of bitumen in benzene, the colour of solvents containing chlorine being affected by light; standard reference curves may thus be compiled for each type of bitumen. A photo-electric method is also described, in which two P.A.I. Westinghouse cells in opposition are equally illuminated by a carbon filament lamp rich in infra-red rays. One of a pair of similar cells containing benzene and a solution of the bitumen, respectively, is placed between each cell and the source of light, and the deflection of a microammeter in the cell circuit is noted; this is compared with the value obtained for the standard type of bitumen. The mineral matter in a Trinidad Epuré is an important indication of purity, because the portion passing a 200-mesh sieve contains, after ignition, approximately 19·0 per cent. of aluminium oxide. It is removed by placing the sample in a brass tube which is closed at the lower end with 200-mesh gauze and immersed in a solvent which may subsequently be removed from the extract by evaporation. The residue is ignited, silica is removed in the usual way by treatment with hydrochloric acid, and iron is separated by electrolysis of the acid solution over a mercury cathode. Aluminium may then be precipitated by means of a 2 per cent. solution of 8-hydroxyquinoline in 1·0 *N* acetic acid in the presence of an excess of ammonium acetate at 65° C. The usual gravimetric procedure is then followed, corrections being applied if a filler containing alumina (*e.g.* Portland cement) is present. The acid value is also a useful means of identification, and is best determined by the method used by the Royal Dutch Shell Group:—The weighed sample (5 to 7 g.) is fluxed with a suitable quantity (*e.g.* 5 ml.) of warm transformer oil or pale spindle oil of low acid value, 100 ml. of ethyl alcohol being then added and the mixture boiled under a reflux condenser for 30 minutes. It is then cooled and titrated with 0·1 *N* sodium hydroxide solution, with 3 ml. of a 3 per cent. solution of alkali blue 6B in alcohol as indicator, allowance being made for any blank on the reagents. Typical acid values (expressed as mg. of potassium hydroxide per 1 g. of sample) are:—Trinidad Epuré, 6·3; Panuco asphaltic bitumen, 0·5; R.O.P. asphaltic bitumen, 0·2; Triniflux, 0·8; Texaco Flux, 1·0; a mixture of Trinidad Epuré and Triniflux (80+20), 4·5. Care must be taken in interpreting results from finished asphalts, because high temperatures or mixing conditions may decrease the acid value. Therefore, although a high value denotes the presence of Trinidad Epuré, a low value does not necessarily prove that it is absent. Portland cement as a filler is often substituted partly or wholly by ragstone or limestone. The former can be detected in the fine material, separated as described above, by the presence of silica and the typical green grains of glauconite (a hydrated silicate of iron, potassium and aluminium), and the latter by a carbon dioxide determination. If Portland cement is present, the fine material gives a red colour with water and phenolphthalein. The substitution of granite by limestone, shingle or slag is detected by dissolving out the bitumen and examining the clean aggregate. Asphalt rock is specified (B.S.S. No. 596, Part 5) as the material to be used in conjunction with an asphalt cement in the manufacture of mastic asphalt, and fluorescence methods for the examination of such products are now available (*cf.* ANALYST, 1935, **60**, 493). J. G.

Determination of Mercury in Iodinated Organic Compounds. R. B. Sandin and E. T. Margolis. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 293–294.)—Spacu's method (*Z. anal. Chem.*, 1932, **89**, 188), in which mercury is determined in presence of iodide by precipitation with a copper sulphate propylenediamine reagent, was adopted. A sample of the organic mercury compound sufficient to yield about 0·3 g. of mercury is decomposed by heating with 3 ml. of nitric acid in a sealed tube, as in the Carius method for halogen determination. The tube is opened and 20 ml. of water, 15 ml. of ammonia and sufficient potassium iodide to dissolve mercuric iodide present, are added. The liquid is diluted to 100 ml., and if free iodine is present, sodium hydroxide is added until the colour is pale yellow. The solution is heated to boiling and an excess of hot reagent [2·5 g. of copper sulphate crystals dissolved in water (amount unspecified) with 2 g. of 70 per cent. aqueous propylenediamine solution added]. After cooling for several hours in ice-water, the blue precipitate is filtered off on a weighed Gooch crucible, and washed 3 or 4 times with water containing 0·1 per cent. of potassium iodide and 0·1 per cent. of the reagent, followed by 3 or 4 2-ml. portions of 90 per cent. alcohol, and finally with 2 to 4 2-ml. portions of ether. The precipitate is dried *in vacuo* and weighed; it contains 21·81 per cent. of mercury. Good results were obtained in tests with tolylmercuric iodide and also samples of various non-iodo organic mercury compounds mixed with di-iodofluorescein. S. G. C.

Inorganic

Diphenylcarbazide as a Reagent for Hydrogen Peroxide. L. N. Lapin. (*Z. anal. Chem.*, 1935, **102**, 418–420.)—The sensitiveness of the perchromic-acid test can be increased very materially by the use of fresh diphenylcarbazide reagent, prepared by dissolving a few crystals in 0·5 ml. of 96 per cent. alcohol and adding 5 ml. of fresh absolute ether (commercial ether, which contains peroxides, cannot be used). The solution to be tested is treated with 2 to 3 drops of 20 per cent. sulphuric acid, 3 to 4 ml. of fresh absolute ether, and 2 to 3 drops of 0·01 *N* dichromate solution, and shaken. The ethereal layer is left to clear, and treated with 2 drops of the carbazide reagent, when a pinkish-violet tinge is given by a trace of perchromic acid not detectable by the blue colour of the ether. The limit of sensitiveness is stated to be 5γ in 5 to 10 ml. W. R. S.

Rapid and Exact Method for the Determination of Mercury. A. Augusti. (*Gazz. Chim. Ital.*, 1935, **65**, 689–693.)—When a solution of mercuric chloride or other mercuric salt is treated with an alkali chromate or dichromate and then with ammonia, the mercury is quantitatively precipitated as mercurio-ammonium chromate, $(Hg_2N)_2CrO_4, 2H_2O$. This precipitate dissolves in potassium iodide or sodium thiosulphate solution, giving $K_2(HgI_4)$ or $Na_2[Hg(S_2O_3)_2]$, together with ammonium chromate and 8 molecules of alkali hydroxide per molecule of the precipitate. Titration of the alkali yields a measure of the mercury present. A definite volume of the mercuric solution is treated, in a centrifuge tube, with a few ml. of potassium chromate or dichromate solution (either *N* or 0·1 *N*, according to the amount of mercury present) and then, drop by drop, with 10 per cent. ammonia solution until the reaction is distinctly alkaline. After some minutes the tube is centrifuged. The liquid is decanted, and the precipitate is washed several times with water, with intermediate centrifugation and decantation, and ultimately dissolved in a concentrated solution of either potassium iodide or sodium thiosulphate, and the liquid is titrated with standard oxalic acid in presence of litmus or phenolphthalein or with a mineral acid with one of the same indicators or with methyl orange: 1 ml. of 0·1 *N* acid ≡ 0·01003 g. of Hg. If the mercuric salt is in the solid form, it is dissolved, in the centrifuge tube, in water or in the minimum quantity of dilute hydrochloric or nitric acid. Mercurous salts must be oxidised beforehand. T. H. P.

Colorimetric Determination of Orthophosphate in Presence of Pyro- and Metaphosphate. K. Boratynski. (*Z. anal. Chem.*, 1935, **102**, 421–428.)—Orthophosphate is the only phosphorus compound answering to the molybdenum-blue test; hence its colorimetric determination is based upon that reaction, due care being taken to depress the rate of hydrolysis of pyro- and metaphosphate. Two reducing agents were used by the author: 1.2.4-aminonaphtholsulphonic acid, and *p*-methylaminophenol sulphate, preferably the latter, as its solution is quite colourless; either reagent contained 0·5 g. of the compound in 195 ml. of 15 per cent. sodium bisulphite, and 5 ml. of 20 per cent. sodium sulphite, solution. The molybdate reagent was a 2·5 per cent. solution of ammonium molybdate in 5 *N* sulphuric acid.

The solution to be tested, diluted to 75 ml., is treated with 10 ml. of molybdate solution, and 4 of the first or 10 of the second reducing agent, and the volume is adjusted to 100 ml. The flasks should be kept for 10 minutes at 25° C. in a thermostat, then for 5 minutes at 15° C., and compared in a colorimeter with a standard (potassium dihydrogen phosphate) prepared in the same manner and at the same time. The method gave accurate results with pure orthophosphate solutions. In presence of *pyrophosphate*, it was found that the determination was correct up to a certain concentration of pyrophosphate, above which the apparent orthophosphate content progressively decreased. The irregularity was found to be related to the quantity of molybdate added, and disappeared upon addition of sufficient molybdate solution. This is explained by the observation that a yellow solution of phosphomolybdic acid is decolorised by the addition of sufficient pyrophosphate, pointing to the formation of a more stable pyrophosphoric complex which is not reduced under the above conditions. When an excess of molybdate is added, it becomes available for the formation of the reducible orthophosphate complex. The author's tests point to a molecular P_2O_5 (*pyro*): MoO_3 ratio of 1 : 6, which must be exceeded by suitable addition of molybdate reagent for the formation of the ortho-complex. *Metaphosphate* was found not to interfere, even in substantial quantities, 3 mg. of orthopentoxide being accurately determined in presence of 100 mg. of metapentoxide; 500 mg. of the latter caused a negative error of about 10 per cent. The determination in presence of *pyro- and metaphosphate* is best carried out in solutions containing not more than 0·025 g. of pentoxide (*meta*+*pyro*) in 100 ml., at which concentration the hydrolytic formation of orthophosphate from the pyrophosphate is almost negligible. W. R. S.

Detection of Potassium by means of Zinc Cobaltinitrite. J. Adams, M. Hall and W. F. Bailey. (*Ind. Eng. Chem., Anal. Ed.*, **1935, 7, 310–311.**)—Zinc cobaltinitrite precipitates potassium, and sodium may be subsequently tested for in the filtrate by the zinc uranyl acetate method. The zinc cobaltinitrite reagent may be prepared by passing a rapid stream of nitrogen oxides (made by acting on copper with nitric acid) for 45 to 60 minutes through a solution saturated with both cobalt acetate and zinc acetate; the resulting dark brown solution is stoppered and decanted from any precipitate formed after standing overnight; the reagent keeps well when tightly stoppered to prevent loss of nitrogen oxides. *Method.*—To the solution from the alkaline earth group, free from barium, arsenate, phosphate or ammonium salts, an equal volume of the reagent is added, and the mixture is kept for 15 minutes; the formation of a yellow precipitate indicates potassium. Tests of sensitiveness showed that 0·4 to 0·6 mg. of potassium per ml. was the smallest amount detectable; 1 mg. per ml. gave a precipitate immediately. Sodium in amounts up to 50 mg. per ml. was without effect. After removal of 50 mg. per ml. of potassium, 3 mg. per ml. of sodium could be detected by the zinc uranyl acetate method, or 1 mg. per ml. of sodium after the removal of 10 mg. per ml. of potassium. S. G. C.

Determination of Alkalis in Felspar. E. W. Koenig. (*Ind. Eng. Chem., Anal. Ed.*, **1935, 7, 314–315.**)—The Berzelius method has been modified to avoid the introduction of sulphuric acid. To the sample (0·5 g., 150-mesh) is added an excess of hydrofluoric acid, and the solution is evaporated to dryness on the water-bath. The residue is extracted with water, and the whole is transferred to a 100-ml. beaker containing 2·5 g. of pure calcium oxide and boiled for 5 minutes. This precipitates iron, aluminium, magnesium and fluorine. The liquid is filtered, and the precipitated hydroxides and fluorides are washed with boiling water and discarded. The filtrate is evaporated to dryness after addition of 25 ml. of ammonium carbonate solution [200 g. of ammonium carbonate and 160 ml. of ammonia (sp.gr. 0·9) per l.]. The residue is dissolved in the minimum amount of water and digested with 15 ml. of the ammonium carbonate solution for 15 minutes; the liquid is filtered, and the residue is washed with a little cold water and rejected. The filtrate is treated with 4 drops of ammonium oxalate solution (saturated), digested hot, and evaporated to 50 ml. Any precipitate is filtered off, washed with 1 per cent. ammonium oxalate solution and rejected, and the solution is acidified with hydrochloric acid and evaporated to dryness on the water-bath. The ammonium salts are volatilised by heating at as low a temperature as possible, and the residue of alkali chlorides is dissolved in a little water, any slight precipitate being removed by filtration, and the solution evaporated to dryness in a weighed platinum dish; the salts are just melted, cooled and weighed. Results obtained with several samples of felspar were in close agreement with those furnished by the J. Lawrence Smith method. S. G. C.

Determination of Stibnite Sulphur in Ores. J. A. Tschernikhov and T. A. Uspenskaya. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 309–310.)—The following method is proposed for the determination of sulphur, combined as antimony sulphide in stibnite and low-grade stibnite ores, containing as impurities other sulphides such as galena, copper glance, cinnabar and pyrites. It is probably applicable to mineral double sulphides such as livingstonite, boulangerite and zinkenite. The sample (200-mesh, corresponding with a maximum of 0·04 g. of sulphide sulphur) is extracted by boiling with 20 ml. of 2 *N* sodium hydroxide for 20 to 25 minutes. This dissolves out the stibnite. The liquid is filtered, and the residue of other sulphides, etc., is washed with hot 0·5 *N* sodium hydroxide solution and rejected. The solution is heated with 0·3 to 0·6 g. of aluminium foil, which precipitates the antimony and leaves the sulphur as sodium sulphide. The antimony powder is filtered off, washed with 0·5 *N* sodium hydroxide solution and rejected. To the cooled solution is added a measured excess of 0·1 *N* iodine solution (20 to 40 ml.), previously diluted to 200 ml. with water, and sufficient hydrochloric acid to neutralise the alkali and to leave about 1 to 2 per cent. of hydrochloric acid in excess. The excess iodine is back-titrated with standard thiosulphate, starch being used as indicator. Results of test experiments showed that the method is satisfactory in the presence of mineral sulphides of lead, copper, mercury and iron. Free sulphur and arsenic sulphide interfere in proportion to the amounts present, which are ordinarily slight. S. G. C.

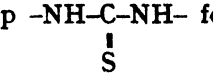
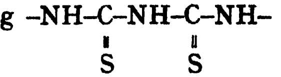
Microchemical

A Pre-heater for use in the Pregl Micro-combustion of Carbon and Hydrogen. W. F. Bruce. (*Mikrochem.*, 1935, 18, 103–105.)—A pre-heater is unnecessary when the apparatus is in constant use, but is very useful when no combustions have been made for several weeks, as it renders it unnecessary to refill the absorption tubes, and oxygen and air from any source may be used; also, larger volumes of gas than the standard amounts may be dealt with without danger of error. The pre-heater consists of a hard-glass test-tube, 1·5 × 12·5 cm., with a side-arm, and it is half-filled with wire-form copper oxide, and wrapped outside with nichrome gauze to the level of the filling. A hard-glass, 5-mm. tube is arranged to penetrate the copper gauze and reach to the bottom of the tube; the other end passes through the rubber stopper and is bent round to give a glass-to-glass contact with the arm of the bubble-counter, to which it is attached with rubber tubing. The side-arm of the test-tube is attached to the 3-way cock of the pressure-regulator of the gases. The apparatus is fixed in the horizontal position, and at the far side of the apparatus, so that it takes up no extra bench space and is not in the way. The end of the glass tube is 1 cm. higher than the stoppered end, to lessen any contact of the hot air with the rubber stopper. A tunnel of asbestos protects the micro-burner which heats the pre-heater, and an asbestos (20 × 30 cm.) shield protects the bubble-counter and rubber connections from any radiation. It is unnecessary to use aged rubber tubing with a pre-heater.

J. W. M.

Micro-volumetric Determination of Methoxyl. D. T. Gibson and T. H. Caulfield. (*J. Chem. Soc.*, 1935, 1419–1420.)—Vieböck and Schwappach (*Ber.*, 1930, 63, 2818, 3207) have described a volumetric modification of Pregl's method which is suitable for 1 to 5 mg. of material, the alkyl iodide being absorbed in bromine, excess of which is destroyed by formic acid, the iodine then liberated on addition of potassium iodide being titrated with sodium thiosulphate solution in the presence of sulphuric acid. The sequence of reactions may be represented as follows:—$CH_3I \rightarrow CH_3IBr_2 \rightarrow IBr \rightarrow HIO_3 \rightarrow 3I_2$. The present authors find that the blank obtained from the absorbing solution is significant, being seriously increased by time, temperature, dilution and exposure to light. An amount of material corresponding with 3 to 10 ml. of 0·02 *N* sodium thiosulphate solution is desirable, and a small flame (instead of a glycerol-bath) should be used for the initial heating, which should be continued for 40 minutes after the b.p. is reached. The absorbing solution is prepared freshly by adding 6 drops of bromine to 18 ml. of 20 per cent. potassium bromide solution; half serves as a blank (the final titration of which should not exceed 0·1 ml.), and 7·5 ml. and 1·5 ml. are placed in the first and second absorption vessels, respectively, all of these solutions (including the blank) being immersed in ice-water in the same vessel. When decomposition is complete, the two absorbing solutions are washed into a conical flask with 45 ml. of 25 per cent. potassium acetate solution, and the mixture is decolorised with 1 ml. of 85 per cent. formic acid; this eliminates the error formerly considered to be due to the formation of bromates produced, owing to the presence of undissolved sodium acetate (cf. *loc. cit.*). The iodine is liberated by the addition of 2 ml. of 10 per cent. potassium iodide solution and 25 ml. of 5 *N* sulphuric acid. The maximum difference between the experimental and calculated values for organic compounds containing 5 to 34 per cent. of methoxyl was 0·47 per cent.; the error for a compound containing 62·0 per cent. of methoxyl was 1·1 per cent. J. G.

Microchemical Test for Choline and its Esters in Tissue Extracts. F. J. Booth. (*Biochem. J.*, 1935, 29, 2064–2066.)—In dilutions of 1 in 1000 down to 1 in 50,000, choline gives a microcrystalline precipitate with Florence's reagent (potassium iodide 1·65 g., iodine 2·54 g., distilled water 30·0 g.). Albumin, glycogen and glucose in 0·5 per cent. solutions do not interfere with the sensitivity of the tests, but the influence of lipoids has not been studied. Acetylcholine does not give a crystalline precipitate, but black globules are seen. After hydrolysis with 1 per cent. sodium hydroxide solution for two minutes at room temperature, followed by acidification with hydrochloric acid to litmus, typical crystals of choline periodide were formed. The water-soluble precursor of choline, which is not precipitated by Staněk's reagent, does not react with the iodine solution until after acid hydrolysis. S. G. S.

Characteristic Atomic Groupings of Bismuth. J. V. Dubský, A. Okáč and J. Trtílek. (*Mikrochem.*, 1935, 17, 332–343.)—A large number of organic compounds which react with bismuth salts have been investigated, and it is found that compounds containing the group  $-NH-\underset{\underset{S}{\|}}{C}-NH-$ form yellow solutions with bismuth salts, whilst the grouping  $-NH-\underset{\underset{S}{\|}}{C}-NH-\underset{\underset{S}{\|}}{C}-NH-$ causes the formation of red precipitates. For testing for bismuth the most useful compound containing the first type of grouping is thiourea, and the most useful containing the second type of grouping is mercapto-sulpho-thiobiazole (named by the authors "bismuthiole").

I. *Thiourea Test.*—The following ions do not interfere with the test:—Pb¨, Cu¨, Hg¨, Cd¨, As¨˙, Sn¨, Ni¨, Fe¨, Mn¨, Al¨˙, Cr¨˙, Zn¨, Ba¨, Sr¨, Ca¨, Mg¨, NH_4˙, K˙ and Na˙. Mercuric salts, however, may be reduced on the surface of the crystal of the reagent to give a black precipitate, and always form a yellow ring round the crystals, whilst mercurous salts give a black stain, and silver salts a brown stain, and must therefore always be precipitated with dilute hydrochloric acid prior to the test. The interfering ferric ions may be reduced with sulphurous acid, and chromates with alcohol. The test is interfered with by the presence of compounds of iron and cyanogen, antimony ions, and strong oxidising agents (not, however, by NO_3' and NO_2'). Antimony salts give a light yellow stain in the conditions of the experiment, but as the reaction is less sensitive for antimony, 10γ of bismuth may be detected in the presence of 66 times the amount of antimony. *Method.*—The slightly acid test solution is tested for silver and mercury with dilute hydrochloric acid. If these elements are present they are precipitated and the test is carried out on the solution. Solutions containing ferric iron or chromate are reduced with sodium sulphite and hydrochloric acid or alcohol. Coloured solutions should be diluted so that a drop of the solution appears almost colourless. A small crystal of thiourea is placed on filter-paper, and a drop of the slightly acid test solution is placed over it. The crystal is coloured yellow at once in the presence of bismuth, and the paper is stained yellow to orange according to the amount present. *Limit of identification*: 1γ of bismuth; *concentration limit*: 1 : 30,000. A positive reaction indicates the presence of bismuth or antimony or both. For comparison, solutions of 0·1 *N* bismuth chloride and 0·1 *N* antimony chloride may be used. If small amounts of bismuth are to be detected in the presence of large amounts of antimony, the separation of the two elements in the sub-group of the hydrogen sulphide group is essential.

II. *Bismuthiole Test.*—This test is especially suitable for the identification of bismuth after its separation from the elements of the hydrogen sulphide group. The basic bismuth salt, which is filtered off in the process of separation, is washed on the filter-paper with a little ammonia and dissolved in a little dilute hydrochloric acid, and this solution is tested for bismuth. Amounts of bismuth too small to be seen on the filter-paper or in the test-tube when precipitated with ammonia, give a positive reaction in the bismuthiole test. The reagent solution is either a 1 per cent. alcoholic solution of the reagent or a solution of 0·7 g. of the reagent in 35 ml. of 0·1 *N* potassium hydroxide solution; both solutions are bright yellow. A drop of the test solution is treated with a drop of the reagent, either in a porcelain crucible or on a spot-plate, when a red to red-orange precipitate forms in the presence of bismuth. *Limit of identification*: 1·2γ of bismuth; *concentration limit*: 1 : 28,000. On filter-paper the colour appears brownish to orange and less red than on a spot-plate, and the sensitivity is less. By adding the reagent to the paper before the test solution an *identification limit* of 2γ of bismuth is attained and a *concentration limit* of 1 : 15,000. The following ions are without appreciable effect on the test:—$Cd^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, and alkali ions. The following ions reduce the sensitivity:—$Ag^{\cdot}$, $Pb^{\cdot\cdot}$, $Hg_2^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Sb^{\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$. Silver ions give a yellow stain on the paper, but 3γ of bismuth may be identified in the presence of 100 times the amount of silver; larger amounts of silver should be removed with hydrochloric acid. The concentration of lead ions should be reduced with hydrochloric acid, when 6γ of bismuth may be identified in the presence of 500 times the amount of lead; under similar conditions 3γ of bismuth may be identified in the presence of 240 times the amount of mercury. Copper salts should be converted into complex cyanides before the test. Antimony salts are very sensitive to the reagent, and give a yellow fleck; 20γ of bismuth, however, may be identified in the presence of 10 times the amount of antimony, owing to the formation of the precipitate in different zones on the filter-paper. In the presence of stannous ions 12γ of bismuth can be recognised in the presence of 200 times the amount of tin. J. W. M.

Cerimetric Titration of Small Amounts of Iron, with the use of *αα′*-Dipyridyl as an Indicator. C. J. van Nieuwenburg and H. B. Blumendal (*Mikrochem.*, 1935, **18**, 39–42.)—Standard solutions of cerium sulphate, even at concentrations of 0·002 to 0·015 *N*, are quite stable if protected from direct sunlight. *Indicator solution*: 0·25 g. *αα′*-dipyridyl is dissolved in 50 ml. of water, and 50 ml. of concentrated ammonia are added (this renders the end-point sharper); 5 drops of this are used for about 5 ml. of the ferrous solution. The iron is reduced to the ferrous state by the silver-reductor of Walden, Hannett and Edmonds (*J. Amer. Chem. Soc.*, 1934, **56**, 350), the acid concentration being maintained within the limits 0·5 to 1·0 *N* hydrochloric acid. The silver reductor consists of a tube, 20 cm. long and 7 mm. in diameter, with a small funnel on top and a stopcock and capillary-tube below passing into a small flask with a side-tubulure attached to a pump, by means of which the air is removed to prevent oxidation. Ferric solution of about 20 ml. volume, containing 0·1 to 10 mg. Fe, is passed through the silver reductor once, the vessel being then rinsed twice with 10 ml. of *N* hydrochloric acid and the liquid made up to a definite volume (50 ml.) and titrated with a 0·002 to 0·015 *N* solution of ceric sulphate in *N* sulphuric acid. The end-point is sharp, within one drop, and better than with a titanous solution. Results tend to be slightly low (about 0·5 per cent.), owing to oxidation by the air dissolved in the solution. Therefore for the determination of amounts less than 0·5 mg., a smaller volume and smaller reductor should be used, *viz.* a reductor 10 cm. long and 4 mm. in diameter for the determination of 0·1 to 0·3 mg. of iron in a volume of 5 ml. by means of 0·0015 *N* ceric solution. It is not advisable to use a sulphuric acid solution of ferrous iron, as the colour of the pyridyl complexes develops much better in hydrochloric acid. J. W. M.

Triple Nitrites of the Rare Earths and a Micro-test for Caesium. H. C. Goswami and P. B. Sarkar. (*J. Indian Chem. Soc.*, 1935, **12**, 608–610.)—The following elements of the rare-earth group were found capable of forming triple nitrites of the formula $Cs_2NaR'''(NO_2)_6$: cerium, lanthanum, praseodymium, neodymium, samarium, and gadolinium. The members of the yttrium sub-group do not yield such nitrites. The triple salts crystallise in octahedra; they are sparingly soluble, and the solutions slowly hydrolyse. For their preparation, 10 ml. of 50 per cent. rare-earth nitrate solution were treated with the same volume of 50 per cent. sodium nitrite solution; to the filtered liquid were added 10 ml. of 10 per cent. caesium nitrate solution. The yellow crystals were collected after some hours, drained and washed, first with 10 per cent. sodium nitrite solution, then with aqueous acetone, and lastly with acetone, and dried in a desiccator. The reaction is a sensitive micro-test for caesium, as rubidium and potassium do not form corresponding salts. The reagent is a filtered solution of 3 g. of praseodymium nitrate and 10 g. of sodium nitrite in 100 ml. of water, and is kept in a well-stoppered bottle. A drop of the reagent is placed on a microscope slide and touched with a loop of platinum wire dipped into the nitrate solution to be tested. After some minutes, fine octahedral crystals appear if caesium is present. A magnification ×400 is used; the sensitiveness is stated to be $0{\cdot}04\gamma$. W. R. S.

Collected References. Application of Catalysis in Micro-analysis. R. Lucas and F. Grassner. (*Mikrochem.*, 1935, 17, 237–261.)—Catalysis is applied in qualitative tests for the following elements in certain inorganic radicals and compounds: hydrogen, sulphur, chlorine, iodine, fluorine, phosphorus, arsenic, silica, nitrogen, magnesium, copper, silver, mercury, thallium, titanium, zirconium and thorium, bismuth, vanadium, chromium, molybdenum and tungsten, manganese, iron, nickel and cobalt, and the platinum metals. These tests are briefly described and 73 references are given. Catalysis may also be applied in the following quantitative determinations: hydrogen, water, oxygen, sulphur, selenium, halogens, nitrogen, carbon, copper, silver, manganese, and certain special compounds such as urea. The methods are discussed and 70 references are given. J. W. M.

References to Microchemical Work in 1934, Part I, pp. 1-80. (Appended to *Mikrochem.*, 1935, **17**.)—A list of references to work appearing in 1934 is given in alphabetical order of the authors' names, divided into the following subject headings:—I. *Pure Microchemistry*: (i) General and apparatus, (ii) Inorganic analysis, (iii) Organic analysis, (iv) Preparative chemistry, (v) Physical chemistry. II. *Applied Microchemistry*: (i) Biological chemistry, (ii) Medical and pharmaceutical chemistry, (iii) Mineralogical chemistry, (iv) Technical chemistry. An appendix (12 pp.) contains additions to previous volumes of references appearing in 1932 and 1933. J. W. M.

Physical Methods, Apparatus, etc.

Electroscopic Method for the Detection of Yellow Phosphorus in the Presence of Tetraphosphorus Tersulphide. W. D. Treadwell and C. Beeli. (*Helv. Chim. Acta*, 1935, **18**, 1052–1060.)—The method depends on the measurement of the ionisation of air which accompanies the luminescence emitted by phosphorus during slow oxidation (*cf.* Schenk and Scherf, *Ber.*, 1906, **39**, 1522). The apparatus consists of a vertical cylindrical glass ionisation-chamber (height 14 cm., diameter 4 cm.), to the top end of which is attached the electroscope. At the base is an earthed copper nozzle placed centrally, which conducts into the cylinder, and serves as a mixer for the air saturated with water-vapour and the nitrogen which carries the phosphorus vapour, and it is essential that these do not come in contact before this point. Air is removed from the nitrogen by passing it over a layer of glowing copper filings and then, in fine bubbles, through a mixture of 1 part of 25 per cent. pyrogallol and 6 parts of 60 per cent. potassium hydroxide solutions. It then passes over a "glass-wick" immersed in a water-bath at 40° C.; this is used as a carrier for the substance to be tested, and consists of 1100 vertical glass rods, 50 mm. long and 0·5 mm. thick, which are contained in an outer glass tube. This device has been found preferable to the use of powdered zinc oxide (which is used to remove hydrogen sulphide from the phosphoric vapour before it enters the electroscope), or to pumice ground to pass a 5-mm. mesh sieve, which produces erratic results owing to irregular distribution of the phosphorus and to the effect of the acidity of the powder. The wick is easily filled by capillary action with 2 to 3 ml. of a solution of the sample in carbon disulphide, the bulk of the solvent being removed by evaporation, and the last traces by the passage of the nitrogen. The leaf of the electroscope is brought to a scale-reading of about 15 by means of rubbed sealing wax, and 55 ml. per minute of air saturated with water-vapour are passed through the ionisation-chamber, and are drawn out at the top by means of a water suction-pump. The rate of fall of the leaf (0·03 to 0·04 unit per minute) is deducted from the final value. A measured quantity of 800 ml. of nitrogen is then passed over the phosphorus in 30 seconds, the effluent gas being re-circulated several times according to the amount of phosphorus in the wick (0·1 mg. requires 2, and 0·5 to 15 mg., 4 circulations). Curves are given showing the amounts of phosphorus in terms of the sum of the rates of fall (in scale readings per minute) of the leaf for each circulation (less the blank), and they show a linear relationship for 0·1 to 1·0 mg. of P (total rates of fall 7·8 and 23·4, respectively), and subsequently a curve which is asymptotic to the blank; these enable quantitative results to be obtained. Solutions of phosphorus should be placed in a spiral wash-bottle and the nitrogen passed through at 52 ml. per minute; the method is quantitative for 20 to 60 mg. of phosphorus in 50 ml. of acetylene tetrabromide, but outside this range, or if paraffin oil is used as solvent, the method is only qualitative and is less sensitive than for samples in the solid state. Scale reading-time curves are also given for mixtures (in the solid state) containing 0 to 50 per cent. of phosphorus in the presence of tetraphosphorus tersulphide (total weight 0·2 g.), in which case the nitrogen is circulated 5 times. In all instances there is little change in the scale-reading at first, but this is followed by a very rapid change which gradually becomes slower, although, when the amount of phosphorus is small, the total change in scale-reading is also small, and an almost horizontal line is obtained. The curves show that phosphorus in the presence of the sulphide is evolved more slowly than in the pure state, and that the oxidation of the vapour of the sulphide is activated by the slow oxidation of the phosphorus, probably owing to the formation of ozone by the latter. The method is sensitive to 0·5 per cent. of phosphorus in the mixture. J. G.

Reviews

A SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS. FRANCIS SUTTON. Twelfth Edition. Revised by A. D. MITCHELL, D.Sc., F.I.C. Pp. xvi + 631. London: J. & A. Churchill. 1935. Price 35s.

To open a new edition of "Sutton" may be compared with meeting an old friend after ten years' absence. We may say at once that the new edition looks very well in its new suit of print; that the old healthy spirit of criticism which distinguished the early editions is still alive, and that Time, in the person of the reviser, has dealt very kindly with our old friend.

The general arrangement remains the same. Much new matter has been added, notably a section by Dr. S. Glasstone on potentiometric titration. Many sections have been entirely re-written, and almost every page bears evidence of revision in accordance with recent improvements in methods and technique. Full use has been made of current literature, references being given to papers published in this journal as recently as 1934.

The revision has been well carried out, and the principles of selection and criticism laid down by the author in 1863 are faithfully followed. So much so, that it is difficult, even with long experience of previous editions, to detect the connecting links between the new and the old. This is as it should be.

Many reviews of previous editions have drawn attention to the freedom of this work from errata. Special mention of this feature was made in the review of the third edition, which appeared in the first volume of THE ANALYST in 1876. The present reviewer congratulates himself on having found one error, by the printer, p. 22, last line. Two of the three printer's errors in the previous edition have been corrected and the other deleted.

The reviser lays stress upon his diffidence in undertaking the task of revising a book with a tradition of seventy years behind it; the reviewer shares his feelings in writing this critique, but, with, perhaps, less regard for mere tradition, would like to offer the following thoughts for consideration.

A good start having been made at re-illustration, it is a pity that the idea was not carried further. The old wood-cuts in Part I, for instance, are hardly in keeping with the fine line-drawings that illustrate the new Part V.

In one or two places use is made of the abbreviation for "molar" as applied to a solution. A few words in explanation of the "molar," as compared with the "normal" system, seem to be called for in the introductory section—particularly in view of the popularity of this book among students. On page 14 there is a paragraph that reads as a recommendation for the use of burette-floats. The float as a means of attaining accurate readings has been superseded by carrying the calibration marks round the instrument. This paragraph requires revision or deletion. On p. 16, in the description of the method of using pipettes, the words occur: "The jet is then stroked off the side of the vessel." This is not in accordance with modern practice for instruments calibrated to N.P.L. specifications (*cf.* p. 21). On p. 25, under preservation of unstable standard solutions, mineral oil is first recommended and then stated to be useless. Space might have been saved by the simple statement that mineral oil is worthless for preventing oxidation, and by a reference to the work of Coste.

The standard temperature of calibration for volumetric apparatus and correction tables for use therewith is given as 15° C. This is, in one respect, regrettable, because it puts the twelfth edition out of date before it is fairly launched. On the other hand, it may be regarded as an advantage, in that it will allow a useful period, of say ten years, for replacement by apparatus calibrated at 20° C.; the change in capacity is negligible for most purposes.

A little more space might have been saved by deletion of methods already superseded by new ones which have been included. For example, in the standardisation of permanganate by metallic iron, paragraph (*b*), p. 120, the last sentence reads: "The content of iron in iron wire used may be determined by means of a permanganate solution that has been standardised by sodium oxalate." These words carry their own recommendation for deletion of the whole paragraph.

Those well acquainted with former editions will look for correction of points to which they may have taken exception in the past. By this test it is fairly safe to predict that they will not be disappointed with the revision. As one instance, in the preparation of standard sodium arsenite, alkali hydroxide is now decomposed by excess of acid before the addition of bicarbonate; this piece of revision was long overdue.

The specialist, turning to his own particular subject, will naturally, since it is the way of the specialist, think that he could have done it very much better himself. Let one example suffice. In the description of Lenssen's method for the determination of tin, it is stated that "the method has been almost entirely superseded by the titration with iodine in acid solution." If the word "almost" were deleted, the statement would be nearer the truth. It is in this section, dealing with applied methods of analysis—the section which has made "Sutton" so valuable in the past, and on which the book's future reputation so largely depends—that there would appear to be still room for an extension of the idea that has led to the introduction of the specially written articles on potentiometric titration and gas analysis by Dr. Glasstone and Messrs. Hollings and Thomas, respectively. There must be many, who, after long experience of some particular determination, would gladly avail themselves of an opportunity of imparting their special knowledge for the enrichment of the pages of their old friend "Sutton."

A general survey of the twelfth edition leaves the impression that the new "Sutton" is a new book. Its appearance marks a definite advance in the history of the "least perishable" of Francis Sutton's works (to quote his own words). The reviser, publisher and printer are to be congratulated on a very creditable production.

F. L. OKELL

THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS. By RALPH L. SHRINER and REYNOLD C. FUSON. Pp. ix + 195. London: Chapman & Hall, Ltd. 1935. Price 11s. net.

The subject-matter of this book is presented in the form of a laboratory course for students who already have some knowledge of organic chemistry. Such laboratory courses have become increasingly popular in the last twenty-five years, and the authors fully realise their value in training the student to use his own judgment and in promoting careful observation and correct deduction.

The book is, therefore, not to be regarded as a comprehensive work. It follows lines long recognised as successful in this country, and has proved its worth in the authors' own University of Illinois.

The system described required, first of all, observation of the physical characteristics of an unknown substance, elementary analysis and determination of physical constants. Emphasis is next laid upon the examination of solubility in water, ether, inert solvents, acids and dilute alkali, whereby the substance is assigned to one group and the field of search is narrowed. "Classification tests" are then applied with specific reagents and disclose the presence of "functional groups." Likely substances are selected from lists in the book, or from general literature, and compared with the unknown. The final proof of identity comes from the preparation of derivatives.

The lists of organic substances referred to are contained in a chapter headed "The Selection of Derivatives," which occupies about half the book and includes details of the reactions and properties of about 1,600 substances. The necessity for reference to larger works, such as those of Beilstein, Richter, Mulliken and Clarke, is emphasised, and references to specific compounds dealt with in recent American literature are included.

The book closes with a chapter on the separation of mixtures, a set of problems, and a comprehensive index. The text is interspersed with exercises.

As will be seen from this description, the book follows closely the ideas behind many of the English University courses, and should, therefore, prove an acceptable alternative to similar works in use here. Special praise is due to the authors, publishers and printers for the attractive presentation and the exceptional freedom of the text from misprints. The long tables of data appear to have been equally carefully prepared.

K. A. WILLIAMS

STRUCTURE AND COMPOSITION OF FOODS. By ANDREW L. WINTON, Ph.D., and KATE BARBER WINTON, Ph.D. Volume II: VEGETABLES, LEGUMES, FRUITS. Pp. 904. New York: John Wiles & Sons, Inc.; London: Chapman & Hall, Ltd. 1935. Price 75s.

The authors in this, the second volume of the series, are concerned, as the title indicates, with fruit and vegetables. The reader, having perused it, must be left with a feeling of wonder and surprise that there is so much to say, so much to report, and so much information available regarding the botanical and chemical aspects of these classes of foods.

Part I (475 pages) deals with vegetables, with the carrot, the potato, the parsnip, no less than with the chayote, the winter squash, the velvet bean and the wrinkled pea, whilst Part II (377 pages) is concerned with fruits, well-known kinds, the pineapple, the plum and the apple, together with many which have unfamiliar names such as jack-fruit, soursop and carambola.

Each vegetable or fruit has a section to itself, and the subject-matter is divided into (*a*) a short descriptive note dealing with history and distribution, (*b*) a note on the macroscopic structure, (*c*) a more detailed comment on the microscopic structure, and finally (*d*), a summary of the chemical composition.

Most of the information on the microscopic structure is based on the original work of the authors, and the data thus presented make the book a valuable work of reference.

An extraordinary amount of facts and figures has been collected in connection with the chemical characteristics of fruit and vegetables, but it is surprising that so much of it is comparatively old (many of the references are to work reported 30 or 40 years ago). Perhaps undue emphasis is laid on this work, and not sufficient on that of more recent investigations, which have in many cases explained and often amplified the early results. For example, in the section on apples there is no reference to the influence of the "climacteric."

The number of references is extremely large (400 on a hundred pages taken at random), but there is little mention of modern English work, and few recorded analyses of English fruit. Incidentally, an amusing error is that "Carré" is referred to as "he."

From the chemical, as apart from the botanical, aspect, the volume cannot be considered seriously as a study of fruits and vegetables, and many points of loose expression of chemical facts can be found, chiefly of the type mentioned in the review of the first volume. One feels that the introduction, with a number of statements to which some exception could be taken, gives but an unfair impression of the value of the book, which is considerable.

L. H. LAMPITT

TEXTBOOK OF QUANTITATIVE ANALYSIS. By W. T. HALL. Second Edition. Pp. vii + 350. London: Chapman & Hall, Ltd. 1935. Price 15s. net.

This book is adapted from Volume II (quantitative) of Treadwell and Hall's *Analytical Chemistry*. It may not be generally known that that work was originally a brief textbook written in German for students when Treadwell was teaching at Zürich. It grew in subsequent editions until it became rather a reference book than a students' textbook. In the book under review the translator has reduced the scope in order to supply the course in analytical chemistry given at the Massachusetts Institute of Technology to embryo chemical engineers.

Part I, which occupies 202 pages, represents the work given to students during the first semester. The volumetric work includes acidimetry and alkalimetry, oxidation-reduction methods with dichromate, permanganate and ceric sulphate. The theoretical aspect of these is well discussed, and the use of diphenylamine as indicator with dichromate is described. In the chapter on iodimetry one would have expected a reference to bromide-bromate solution. A chapter is devoted to precipitation methods.

The section on gravimetric analysis contains a good discussion of solubility-product and of some sources of error. A point which impresses the reviewer is the eminently practical outlook displayed in emphasising (pages 170–173) the importance of correct sampling and the references given to the literature of this subject. He doubts, however, the wisdom of encouraging students to use "factors" in chemical calculations. Practical exercises given are determinations of chlorine, iron and sulphur in simple salts, of phosphoric acid in apatite, and analyses of limestone and of Portland cement. Part I concludes with a chapter on the theory of electrolysis and the analysis of brass.

Part II covers methods which, to quote the preface, "have been developed in busy technical laboratories such as those of a steel plant." A chapter on analysis of silicates is followed by descriptions of the determination of the usual elements in steel. Some practical methods of ore analysis (other than dry assay) are dealt with, and chapters devoted to the analysis of bearing metals and to potentiometric titrations, both the hydrogen and the quinhydrone electrode being described.

It will be seen that the book is designed to cover a rather specialised course. This, no doubt, explains the absence of such features as a systematic list of methods for the determination of the leading elements and groups and their separations one from another. Likewise, gas analysis is not dealt with (though one might have expected chemical engineers to need this).

Throughout the book operations are described in considerable detail, and the underlying theoretical principles are well explained. A useful number of references to original papers (not all of them American) are given, and there is a set of problems at the end of each chapter. Some of these are unusually instructive. A student working through this book would attain a very good general grounding in analytical chemistry.

The printing and binding are good, and it is a great advantage that the book "stays put" when laid open on a bench. H. S. Howes

WASSERSTOFF-IONENKONZENTRATION (*p*H). By H. JÖRGENSEN, with an Introduction by S. P. L. SÖRENSEN. Pp. 264. Dresden: Theodor Steinkopff. Price, 15RM. (paper); 16RM. (bound).

The realisation of the importance of hydrogen-ion concentrations, in the control of industrial processes as well as in analytical work, has resulted in the appearance of a number of important books dealing with this subject during the past decade. The present monograph differs from the others in several respects: it is not intended to be exhaustive, for the object of the book is to give a survey of the theory and application of the measurement of hydrogen-ion concentrations likely to be of particular interest to "practical" men ("praktisch-arbeitende Chemiker"). The author says, "apparatus for the determination of *p*H is to be found on expedition ships in the seas around Greenland as well as in the sugar factories of distant tropical islands"; he does not, however, attempt to cover the whole of the material between these two extremes, but has chosen sixty-two typical examples, drawn from industry and agriculture, which illustrate clearly the importance of *p*H control. References to fermentation, baking, sugar, paper, leather, organo-therapy, soil science, milk, confectionery, textiles and dyeing are included, and an attempt is made to systematise the widely differing applications according as the hydrogen-ion concentration affects the process directly, indirectly or in a complicated, hitherto unexplained, manner. Of particular interest to analytical chemists is a ten-page appendix on the significance of *p*H in acid-alkali titrations: the special value of this section lies in the fact that the author has courageously adopted the modern definition of acids and bases, as donors and acceptors of protons, respectively, with gratifying results.

The theoretical principles underlying the determination of hydrogen-ion concentrations are discussed in a brief but clear manner, and the general background of electrochemistry is described sufficiently to permit the subject to be understood by one who has been out of touch with academic chemistry for some time. The author does not aim at giving adequate practical details for determining *p*H values—in fact, the reader is referred to other treatises in this connection. Nevertheless the methods for using the hydrogen and quinhydrone electrodes are explained fully; the treatment of indicator methods and of the glass electrode is, however, not nearly so complete.

A fully indexed list of some 240 selected references completes the text of this interesting book; as the author is a Dane, the German is fortunately simple in style and quite readable. S. GLASSTONE

THE EXTRA PHARMACOPOEIA (MARTINDALE AND WESTCOTT). Vol. II. Twentieth Edition. Pp. 776 and Index 112. London: The Pharmaceutical Press and H. K. Lewis & Co., Ltd. 1935. Price 22s. 6d.

This book is so generally known as "Martindale" that its actual title seems a misnomer, and, whilst we have the British Pharmacopoeia and the British Pharmaceutical Codex as accepted books of reference, it might seem superfluous to publish an Extra Pharmacopoeia, yet it is the multitude of other things to be found in "Martindale" which has made it a necessity for medical practitioners, pharmacists, and analysts, during the past fifty years. When first published in 1883, it was a slim little volume written by a pharmacist and a doctor, and it contained information equally needed by a dispensing chemist and a busy doctor. Many a hospital dispensary possessed a "Martindale," and most doctors who drove a brougham carried the volume with them everywhere, although they seldom possessed or looked at the British Pharmacopoeia; in fact, the book might be considered the strongest link between applied medicine and chemistry. That it has remained so for fifty years is proof of its unfailing usefulness, and when the subject outgrew the space afforded by one small volume, it was arranged to publish it in two parts. After the decease of the original authors, and of the son of Martindale, who succeeded to the task of writing and publishing the book, it was considered to be such a valuable book of reference that the Council of the Pharmaceutical Society acquired the right to the copyrights, and arranged to continue the publication under the direction of an editor (C. E. Corfield) and a Revision Committee.

The volume now published is the first one to appear under the new auspices, and retains in *format* and style the familiar appearance and arrangement of its precursors. It also retains the inconvenience of finding information on a subject in the two separate volumes, and, although this is remedied in Vol. II by an index to both volumes, yet it does not make for ready co-ordination of some of the information.

It was, and still seems to be, the intention that the second volume should give information much more extensive in character than the descriptions of specific drugs and chemicals and their dosage, which are found in Vol. I, and for this reason the book may almost serve as a text-book on some subjects, among which analysis may be considered one of the most important.

Under the heading "Analytical Addenda to Chemicals and Materia Medica in Vol. II," 204 pages are devoted to substances of medical, chemical and pharmaceutical importance, whose names are comprised between Acacia and Zingiber, and a very large amount of information is condensed (perhaps collected would be a better word) in a very small space. The particulars are verified by reference to published information, and for the accuracy of these the present publishers must owe a tremendous debt to the late Dr. W. H. Martindale, and no review could attempt to criticise what must have taken a lifetime to compile and continually revise.

After this important section of the book, there are shorter ones dealing with a variety of subjects, such as:—The Action of Acids on Common Metals, Organic Reagents for Inorganic Analysis, Indicators; then some sixty pages of intensely interesting matter, *viz.*: "Scheme for the recognition of organic chemical substances used in therapeutics," the practical value of which, to almost any analyst, is incalculable, for, in addition to the scheme, the corroborative tests for some 277 substances of unusual nature are given, for which hours of search would be needed if they were sought in ordinary text-books.

The section dealing with the Chemical Tests and Microscopic Methods for the examination of Urine, Blood, Faeces and Stomach Contents, will be of special value for pathological work, and comprises all the most recent technique. For this alone the book will be in daily use in many laboratories.

The chapter on Nutrition is particularly informative, and includes the references to the most recent work and published results, and the section on Vitamins is one of the most helpful summaries of the latest information available.

Milk, Cream, Jam, Bread, and Flour, and Food Colours are all treated lucidly, and the Notes on Water Analysis are almost a treatise on that subject; so also may be described the Bacteriological and Clinical Notes, and the chapters on Sterilisation, Disinfectants, Gas Poisoning, Chemotherapy, Radium, *X*-ray Diagnosis, and Electrotherapy and Actinotherapy.

To many analysts the section on Proprietary Medicines will be of immediate interest, for, since the necessity for use of patent medicine stamps has been withdrawn, the container or label on so many of these preparations has to bear the formula or composition of the contents. The information is nowhere else presented in such an available manner, and if it is not always precise, that is no fault of the authors of the book.

Glossaries in Arabic, Danish, Dutch, French, German, Italian, Portuguese and Spanish will be helpful, and the last words "Yema de huevo" (yolk of egg) precede the Index of 112 pages, wherein is centred the vital secret of the worth of this invaluable book.

If one were asked to describe this "Martindale," it would be correct to state that it was something more than a text-book, a dictionary, a compendium, or a *vade mecum*, and to add that it embodies the life-work of two exceptional men—father and son—to which has been added the results of the Revision Committee, and the help of an editor with unique experience. C. E. Sage

Rubber. Physical and Chemical Properties. By T. R. Dawson, M.Sc., F.I.C., F.I.R.I., and B. D. Porritt, M.Sc., F.I.C., F.R.S.E., F.I.R.I. With a Foreword by Sir Herbert Wright. Pp. 700 + xi. Published by the Research Association of British Rubber Manufacturers. 1935. Price 45s.

This monumental work, produced by the co-operation of the Rubber Growers' Association and the Research Association of the British Rubber Manufacturers, may be said to form a milestone on the road of progress along which rubber technology has of late advanced very rapidly. The intention of the promoters of the book has been to provide a concise record of all the scattered data on rubber, so that not only the rubber technologist but others interested in the applications of rubber, such as engineers, architects and so on, should have such data ready to hand. The authors have not only accomplished this enormous task in a most creditable manner, but have at the same time provided the rubber industry with what it has long wanted, namely, an up-to-date survey of technical literature.

The well-known reference work of Bedford and Winkelmann (*Systematic Survey of Rubber Chemistry*) was published in 1923, whereas the present authors have utilised current literature up to March, 1934. A very large gap has thus been filled and this, in conjunction with the comprehensive subject index provided, should be of great value to the rubber technologist.

As already indicated, however, the book is not intended only for those familiar with rubber technology, but may be strongly recommended to anyone desiring information on the properties of rubber. The published price of 45s., which is very low for such an extensive work, should encourage the use of the book for this purpose.

Some idea of the contents of the book will be obtained from the following sectional headings:

	PAGES
Introduction (Explanatory).	
Latex.	
Chemical Properties, Colloid Properties, Physical Properties, etc.	1–15
Coagulum	16
Raw Rubber.	
Chemical Properties. Constitution, Composition, Isomeric Derivatives, Tackiness, etc.	17–35
Physical Properties. Mechanical, Thermal, Electrical and Optical Properties, etc.	36–78
Vulcanising Properties. Duplicability in Vulcanisation and Testing, Properties of Vulcanisates as affected by factors in the preparation of Raw Rubber, etc.	79–177
Soft Vulcanised Rubber. Chemical Properties.	
Changes due to natural ageing. Changes due to heat and heat ageing, Changes due to action of light, etc.	178–210

	PAGES
Soft Vulcanised Rubber. Physical Properties.	
Tensile Stress-Strain Properties, Permanent Set, Volume Change due to Extension, Energy Relations, etc.	211–484
Sponge and Cellular Soft Rubber.	
Chemical Properties. Physical Properties	485–491
Sponge and Cellular Rubber.	
Sponge Rubber. Microporous Rubber, Cellular Rubber	492–493
Hard Rubber.	
Chemical Properties. Specific Gravity, Stress-Strain Properties, Resilience, Hardness, etc.	493–520
Conversion Tables and Factors	521–530
Methods of Analysis and Testing.	
Latex, Analysis, Testing Soft Vulcanised Rubber, Testing Hard Rubber	531–547
Specifications for Rubber Goods.	
United Kingdom, United States of America, Index of Rubber Goods Specified	548–565
Associations and Institutions connected with the Rubber Industry	566–573
Selected Bibliography of Rubber Literature	574–582
Bibliography of Authorities Cited	583–598
Glossary	599–603
Index of Mixings.	
Ingredients in the Mixing	604–642
Index of Subjects	643–690
Index of Names	691

It will be seen that the largest section is that dealing with the properties of soft vulcanised rubber, the applications of which include all the most important uses of rubber. The properties of latex, raw rubber, hard rubber (vulcanite) and sponge rubber are also fully covered, and conversion tables, methods of analysis and testing, specifications, list of Associations, bibliographies of the literature and authorities cited, glossary, index of mixings and subject and name index are provided.

The subject-matter is presented in tabular form with suitable explanatory headings. The scheme of arrangement of the tables, etc., follows that of the International Critical Tables, the rubber section of which is by Dr. G. S. Whitby, to whom acknowledgment is made in the foreword. Ready reference to any section of the present work can be made by consulting the comprehensive indexes provided.

The section dealing with methods of analysis and testing has been based, as far as possible, on the publications of British and foreign standardising authorities, and is a valuable feature of the book. In passing, it may be noted that no tests for traces of copper or manganese have been included, and, as these are of great importance in connection with the examination of damaged or deteriorated rubber, they might usefully find a place in this section.

A further point noted by the reviewer is the apparent absence of any data on the extreme effects of heat on raw rubber, such as, for example, the properties of "molten rubbers," destructive distillates, etc. Apart from these two points, no part of the book that the reviewer has so far consulted has been found lacking.

To conclude, this work is the most comprehensive summary of the properties of rubber ever published. It is essentially a reference book, but, as such, it should be found wherever the properties of rubber are likely to be of interest. It is hoped that its publication will materially assist in that dissemination of information on this unique substance which is so desirable for the purpose of securing its widest application.

W. H. STEVENS

I. A. R. I. 75.

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